

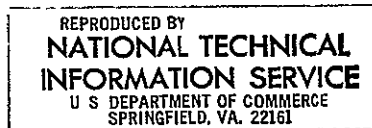
(NASA-CR-147479) DEVELOPMENT OF A  
PROTECTIVE DECORATIVE FIRE RESISTANT LOW  
SMOKE EMITTING, THERMALLY STABLE COATING  
MATERIAL Final Report (Institute for  
Research, Inc.) 80 p HC \$5.00 CSCI 11D G3/24 18408  
N76-18234  
Unclas

N76-18234

Final Report  
DEVELOPMENT OF A PROTECTIVE  
DECORATIVE FIRE RESISTANT  
LOW SMOKE EMITTING, THERMALLY  
STABLE COATING MATERIAL

Contract No.: NAS-914726

PRICES SUBJECT TO CHANGE



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January 30, 1976

## DEVELOPMENT OF PROTECTIVE, DECORATIVE AND EASILY CLEANED COATING MATERIAL

### PURPOSE:

The purpose of this program is to provide the National Aeronautics and Space Administration with the efforts necessary to formulate and develop a fire-resistant, low smoke emitting, thermally stable, easily cleaned coating material. The coating is to be used for covering substrate panels, such as aluminum, silicate foam, polymeric structural entities, etc., all of which are applied in the aircraft cabin interior and thus subject to the spillages, scuffing, spotting and the general contaminants which prevail in aircraft passenger compartments.

### INTRODUCTION:

The research program involved the development of suitable electrocoatings and subsequent application to nonconductive substrates. Substrates investigated were plastics or resin-treated materials such as FX-resin (phenolic-type resin) impregnated fiberglass mat, polyphenylene sulfide, polyether sulfone and polyimide-impregnated unidirectional fiberglass.

For electrocoating, the paint emulsion must contain charged paint particles colloidally suspended in the carrier and the solvent. For anodic electrodeposition, the paint particles must be negatively charged. The object to be coated is made the anode in the electrochemical system. Hence, to electrophoretically deposit a coating on a nonconductive substrate, the surface has to be rendered conductive first. Several approaches were tried in this study:

- 1) electroless plating to deposit a thin metallic film on the non-metallic substrate.

- 2) incorporation of metal in the resin formulation
- 3) inductive charging of the substrate
- 4) sizing with conductive coatings

In the formulation of the electrocoating emulsion, polyvinylidene salts, epoxies, acrylics and epoxy-acrylic cross-links were investigated for suitability as carriers. Different intumescent agents were incorporated to promote thermal stability and fire retardancy. Polyvinylidene fluoride (Kynar) was found to give increased abrasion and stain resistance of the coatings, and is the preferred fluoropolymer.

A 4' x 4' panel of polyimide-impregnated unidirectional fiberglass was coated with the preferred coating and evaluated for physical and chemical properties.

Phenolic type resin was found to be a slightly more satisfactory substrate for the process and the preferred coating material, however, the coatings on the polyimide type substrate are also compatible with the electrophoretic process as well as the various paint formulations.

## EXPERIMENTAL

I. Electroless Plating to Render the RX-Resin (Phenolic) Impregnated Fiberglass Conductive. The Schematic is shown in Figure 1.

### A. Copper Plating

#### 1. Solvent Swelling

##### a. Preparation of Solution

<u>Part I</u>	<u>% Weight</u>
kaolin	0.5%
dioxane	3.0%
p-toluene sulphonic acid	0.3%
<u>Part II</u>	
perchloroethylene	96.2%

Add Part II to Part I immediately before use.

##### b. Process Sequence

- (1) Immerse material to be plated in solution 10-60 seconds at a temperature of 85-120°C.
- (2) Immediately transfer to a hot oven maintained at 100-120°C. (1 minute at 120°C. is maximum).
- (3) Rinse in deionized water maintained at 70-80°C.

#### 2. Chemical Etching

##### a. Preparation of Solution

- (1) Potassium hydroxide (10%) -- dissolve 10 g. potassium hydroxide in deionized water to make 100 ml. solution
- (2) 85% phosphoric acid, chemically pure grade reagent

##### b. Etching

- (1) Potassium hydroxide etching - immerse in the potassium hydroxide solution for 2-3

minutes at 60°C.

- (2) Phosphoric acid etching - immerse for one minute at 60°C.

c. Rinse thoroughly with deionized H<sub>2</sub>O

3. Sensitizing

a. Preparation of Sensitizing Bath

Stannous Chloride	10 g.
Hydrochloric Acid, conc.	40 ml.
Deionized H <sub>2</sub> O to make one liter solution	

b. Put the etched pieces of fiberglass in the sensitizing bath for 1-3 minutes at room temperature

c. Rinsing

Transfer immediately to a beaker containing a milky rinsing solution (deionized H<sub>2</sub>O with trace amounts of SnCl<sub>2</sub>).

4. Activating

a. Silver-based Activating Bath

Silver Nitrate	2.5 g.
Ammonium hydroxide, conc.	10-20 ml.
Deionized H <sub>2</sub> O to make one liter solution	

pH of solution	9-13
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Dissolve the silver nitrate in a small volume of H<sub>2</sub>O by stirring. After complete solution, add the ammonium hydroxide slowly, stirring continuously. A chocolate brown color develops which darkens as more ammonium hydroxide is added. Continue adding the ammonium hydroxide until the solution clears up completely. Measure the volume of the solution at this point

and add the concentrate to a beaker containing enough deionized  $H_2O$  to make a liter of activating bath.

- b. Immerse in activating bath at room temperature.
  - c. Rinse the fiberglass in running cold  $H_2O$  and follow with a spray rinse to make sure that no trace of catalytic metal is left behind with the fiberglass.
5. Chemical Plating

a. Preparation of Plating Solution

Part A

Sodium potassium tartrate	170 g.
Sodium hydroxide	50 g.
Copper sulfate	35 g.
Sodium carbonate	30 g.
Tetrasodium ethylene diamine	
Tetraacetic acid	
(0.45 g/100 ml. solution)	20 ml.
Deionized $H_2O$ to make one liter solution	

Part B

Formaldehyde, 37% by weight

- b. Mix 5 parts A to 1 part B just before plating
- c. Let the fiberglass stand in the plating solution for 20-60 minutes at room temperature, depending on thickness of copper film desired. The deposition rate is 1-1.2 mil/hour at room temperature.

B. Nickel Plating

- 1. The procedure is essentially the same except the chemicals for the activating step and the plating

step are different.

a. Activating Solution

Palladium nitrate	0.25 g.
Hydrochloric acid, conc.	10.0 ml.
Deionized water to make one liter	

b. Etching Solution

Potassium Dichromate	5.0 g.
Sulfuric acid, conc.	450.0 g.
Phosphoric acid, conc.	150.0 g.
Deionized water	350.0 g.

II. Description of Experimental Set-Up

One-liter beakers were used to contain the different baths and rinses. For temperature control, the solution baths were set on heating mantles controlled by Powerstat rheostats. The top part of the baths (above the heating mantle) was wrapped with fiberglass insulation and aluminum foil.

III. Preparation of White FX-Resin Impregnated Fiberglass by Electrodeposition with Polyvinylidene Fluoride (Kynar)

A. Solution Preparation (0.5%)

Kynar 201 (Pennwalt)	2.5 g.
Acetone	497.5 g.

The Kynar powder was added to the acetone and stirred for one hour. Not all the Kynar dissolved but the presence of excess solid allowed more electrodeposition experiments to be run with the same solution.

B. Experimental Set-Up

The schematic diagram of the apparatus is shown in Figure II.

The electrodeposition system consists of the power supply, volt meter, current meters, electrodeposition bath and a timer.



The power supply consists of four regulated d.c. power supply units connected in parallel. The number of power supply units used varies depending upon the current developed in the bath. The power supply is coupled with a high precision a.c./d.c. voltmeter so that an accurate measurement of the voltage applied to the electrodes can be made. The switch that controls the imposition of d.c. voltage across the electrodes also activates a timer to get a simultaneous record of electrodeposition time. For current measurements, a milliammeter and/or a microammeter are used. For electrophoretic systems where high currents are developed from the electrode reactions, the microammeter is taken out of the circuit.

The electrodeposition bath consists of a pyrex beaker (400 - 2000 cc, depending upon the size of the piece to be coated) and a Teflon-coated stirring bar mounted on a magnetic stirrer. For temperature control, the beaker is wrapped with heating tape. A rheostat regulates the heating rate.

The anode is the sample to be plated (if conductive). For non-conductive plastics, a piece of aluminum slightly larger than the sample is used as the back plate. The preferred cathode is lead. For a one-inch electrode separation, an insulated bracket is used to mount the electrodes. The bracket allows the electrodes to be moved in and out of the bath without changing the separation distance. For larger electrode separation, the insulated bracket is replaced by two clamps.

The electrodes are cleaned with a steel brush and rinsed in acetone and then cleaned ultrasonically

in carbon tetrachloride to insure complete removal of contaminants from the surface. The pieces to be coated are rinsed in acetone.

C. Electrodeposition Experiments with Conductive Fx-Resin Impregnated Fiberglass.

Pieces of the Fx-resin impregnated fiberglass rendered conductive by electroless copper plating were electroplated at 200 volts and 300 volts for three minutes each.

IV. Experiments to Prepare White Conductive Fx-Resin

A. Resin Formulations

The Fx-resin (made by mixing two components - 85% A and 15% B which is the curing agent) was mixed with different and varying proportion of white pigments and metal powders. The formulations and the resultant properties of the resinous products are shown in Table I.

B. Preparation of Fx-Resin Impregnated Fiberglass

100 grams A, 15 grams B, and 2 grams aluminum powder were mixed in a blender until homogeneous.

The mixture was poured on a thin layer of fiberglass mat. The resin-treated fiberglass was cured at 200°F. for one hour. The cured substrate was cut into pieces, about 2" x 1" size for electrodeposition experiments.

V. Electrocoating with Paint Emulsion Based on Polyvinyl Salts

A. Electrocoating Paint Emulsions with Polyvinylidene Chloride (PVC) as Charge Carrier was prepared as follows:

PVC Paint Formulation IW\*

<u>Components</u>	<u>% by wt.</u>
Polyvinylidene Chloride (Daran 211, 60% solids)	40.0

Note: \*W = White

Deionized Water	40.0
Titanium Dioxide	15.0
Kynar 201	5.0
G.E. Antifoam 60	2 drops

#### PVC Paint Formulation IIW

<u>Components</u>	<u>% by wt.</u>
Polyvinylidene Chloride, 60% solids	39.99
Deionized Water	39.99
Titanium Dioxide	10.0
Moly White 101 (Sherwin Williams)	5.03
Kynar	5.0
Antifoam 60 (G.E.)	2 drops

- B. A Polyvinyl Acetate (PVA)-based Electrocoating Paint was also formulated:

#### PVA Paint Formulation IW

<u>Components</u>	<u>% by wt.</u>
Polyvinyl Acetate (Airco 880)	20.0
Sodium Tripolyphosphate	23.0
Deionized Water	39.5
Titanium Dioxide	9.0
Dichloroethane	7.0
Triethyl Phosphate	0.7
Lecithin	0.4
Antifoaming Agent (Dow Corning D13-110)	0.4

The formulations were homogenized in a blender for five minutes, poured into the electrodeposition vessel and allowed to stand at room temperature for a few hours to defoam. If left overnight to complete defoaming, the formulations were kept in the refrigerator. The electrodeposition experiments are summarized in Table II.

#### VI. Electrocoating with Epoxy-based Paints

Several paint formulations were made up and tested

for compatibility and suitability with different metallic substrates.

A. Solvent-Dispersed Epoxy

Formulation IEW\*

<u>Components</u>	<u>% by wt.</u>
<u>Part A:</u>	
Epoxy (Shell Epon 1007, 25% solids in MIBK)	47.96
Talc Powder	15.75
Silica-free Titanium Dioxide	11.02
Moly White 101	5.73
Sodium Tripolyphosphate	0.64
Methyl Isobutyl Ketone (MIBK)	3.58
M-Pyrol	4.22
Kynar 201	0.72
<u>Part B:</u>	
Ethylamine	9.31
N-Butyl Alcohol	1.07

Part A was homogenized in a blender for five minutes. Part B was mixed manually and then added to Part A. The mixture was homogenized for a few minutes.

Formulation IIEW

<u>Components</u>	<u>% by wt.</u>
<u>Part A:</u>	
Epoxy Resin (Epon 1007, 25% solids in MIBK)	41.78
Talc Powder	13.72
Silica-free Titanium Dioxide	9.67
Moly White 101	4.99
Sodium Tripolyphosphate	0.56
Methyl Isobutyl Ketone	3.12
M-Pyrol	19.33

Note: \*EW = Epoxy-based, White

Kynar 201	2.34
Antifoam 66	4 drops

Part B:

Versamid X 265-WR70 (General Mills)	4.02
N-Butyl Alcohol	0.47

The mixing procedure is the same as in IEW.

Formulation III EW

<u>Components</u>	<u>% by wt.</u>
<u>Part A:</u>	
Shell Epon 829 (25% solids in MIBK)	39.60
Talc Powder	13.00
Titanium Dioxide (TiO <sub>2</sub> )	9.16
Moly White 101	4.73
Sodium Tripolyphosphate	0.53
Methyl Isobutyl Ketone	2.96
M-Pyrol	18.32
Kynar 201	2.22
Antifoam 66	2 drops
<u>Part B:</u>	
Versamid X 265-WR70	8.49
N-Butyl Alcohol	0.99

The A components were ball-milled together for one hour. Components of Part B were mixed and stirred manually and then added to A and ball-milling was continued for another 30 minutes.

Formulation IV EW

III EW was modified by addition of intumescent agents.

<u>Components</u>	<u>% by wt.</u>
Formulation III EW	81.2
Ammonium Polyphosphate	12.0
Dipentaerythritol	3.2
Melamine	3.6

The mixture was ball-milled for one hour.

#### Formulation VEW

Modification of IIEW to add conductive property

<u>Components</u>	<u>% by wt.</u>
Formulation IIEW	98.63
Al flakes	1.37

The mixture was homogenized in the ball mill for one hour.

#### Formulation VIEW

Water-Reducible Epoxy-Resin Coating

To prepare a water-based electrodeposition vehicle, an epoxy resin was modified using the following procedure:

<u>Chemical Reactant</u>	<u>% by wt.</u>
Shell Epon Resin 829	20.14
Bisphenol A	5.44
Benzoic Acid	14.39
Benzyl dimethylamine	0.03
Xylene	1.60
Linseed Oil Fatty Acids	34.37
Stannous Octoate	0.007
Maleic Anhydride	4.00
Oxitol	20.02

The liquid epoxy resin and the bisphenol A were mixed in a 2-liter pyrex resin reaction vessel and heated to 280°F. The temperature was maintained for about 20 minutes. Benzyl dimethylamine, benzoic acid and xylene were added to the mixture, the temperature raised to 392°F, and maintained for four hours. The stannous octoate was then added, followed by the linseed oil fatty acids. The mixture was heated to 520°F and maintained for four hours. The mixture was cooled to 375°F and the maleic anhydride was added. The temperature was raised to 400°F, held for one hour, followed by cooling to 225°F and finally thinning

with methyl oxitol to 80% solids content.

The pigment concentrate was prepared from the following components:

<u>Components</u>	<u>% by wt.</u>
Titanium Dioxide	19.15
Epoxy Vehicle (80% solids)	
Grind	12.77
Let Down	47.13
Ethomeen T-25 (Armour)	0.11
Methyl Oxitol	5.74
Benzylamine	4.15
Deionized H <sub>2</sub> O	10.96

The titanium dioxide was dispersed in the grind portion of the epoxy vehicle and the ethoxylated fatty amine (Ethomeen T-25) by milling in a colloid mill for 30 minutes. The resultant paste was reduced with the let down portion of the epoxy vehicle with stirring. The remaining components were added gradually in the sequence above. The pigment concentrate was milled for another hour and allowed to stand overnight. The final paint emulsion was made by diluting the pigment concentrate to get 10% solids. The resin modification of the epoxy resin was incomplete. The pigment concentrate blended with deionized H<sub>2</sub>O with difficulty so a mixture of 600 ml. methyl oxitol, 500 ml. acetone and 686 ml. deionized water was used for dilution.

B. Water-based Epoxy Electrocoating Emulsion

Formulation VII EW

<u>Components</u>	<u>% by wt.</u>
<u>Part A:</u>	
Deionized H <sub>2</sub> O	9.30
Natrosol 250 HR	0.09
General Mills Gen Epoxy M205	9.30

Part B:

Deionized H <sub>2</sub> O	30.14
Natrosol 250HR	0.08
Tween 20	0.86
TiO <sub>2</sub>	14.26
Kynar 201	0.62
Aurasperse W4123	trace
Antifoam 66	2 drops
Antifoam 70	2 drops
Curing Solution	
Versamid 5201-HR65	16.75
G.E. Antifoam 66	2 drops
G.E. Antifoam 70	2 drops
Deionized Water	18.60

The Natrosol was dispersed in the weighed quantity of deionized H<sub>2</sub>O. The Gen Epoxy M205 was then added slowly and the mixture stirred (with a magnetic stirrer) for 45 minutes.

The water in Part B was weighed into a colloid mill and the Natrosol dispersed into it. The rest of the components were added slowly with stirring following the above sequence. The mixture was ball-milled for 30 minutes.

A was added to B slowly. This is Component I. The curing solution components were subsequently added with stirring to Component I to make the electrocoating emulsion.

The mixture was allowed to stand to defoam. To lengthen the pot life of the emulsion, refrigerate when not being used. Addition of deionized water helps control the viscosity of the emulsion and prolongs the curing of the epoxy, hence the pot life of



the emulsion.

C. Preparation of Colored Epoxy-based Electrocoating Emulsions

1. Red

Formulation IER\*

<u>Components</u>	<u>% by wt.</u>
<u>Part A:</u>	
Epon Resin (25% in MIBK)	45.95
Red Iron Oxide	6.08
Ferric Acetoacetate	4.05
Igepal 880, 20% W/V	9.46
M-Pyrol	9.46
Deionized H <sub>2</sub> O	9.46
MIBK	10.81
<u>Part B:</u>	
Versamid X 265-WR70	4.05
Butyl Alcohol	0.68

Formulation IIER

<u>Components</u>	<u>% by wt.</u>
<u>Part A:</u>	
Epon Resin (25% in MIBK)	43.04
Red Iron Oxide	5.70
Ferric Acetoacetate	10.13
Igepal 880, 20% W/V	8.86
M-Pyrol	8.86
Deionized H <sub>2</sub> O	8.86
MIBK	10.13
<u>Part B:</u>	
Versamid X 265-WR70	3.80
Butyl Alcohol	0.63

Note: \*ER = Epoxy-based, Red

### Formulation IIIER

<u>Components</u>	<u>% by wt.</u>
<u>Part A:</u>	
Epon Resin 1007 (25% in MIBK)	65.38
Ferric Acetoacetate	14.42
Igepal 880, 20% NV	13.46
<u>Part B:</u>	
Versamid X 265-WR70	5.77
Butyl Alcohol	0.96

### Formulation IVER

<u>Components</u>	<u>% by wt.</u>
Epon Resin 1007 (25% in MIBK)	62.96
Red Iron Oxide	8.33
Molybdate Orange	9.26
Igepal 880, 20% NV	12.96
Versamid X 265-WR70	5.56
Butyl Alcohol	0.93

### Formulation VER

<u>Components</u>	<u>% by wt.</u>
<u>Part A:</u>	
Epon Resin 1007 (25% in MIBK)	41.79
Talc	13.80
Ferric Acetoacetate	14.59
Sodium Tripolyphosphate	0.55
MIBK	3.11
M-Pyrol	19.32
Kynar 201	2.35
Antifoam 66	2 drops
<u>Part B:</u>	
Versamid X 265-WR70	4.02
Butyl Alcohol	0.47

### Formulation VIER

<u>Components</u>	<u>% by wt.</u>
<u>Part A:</u>	
Epoxy Resin 1007 (25% in MIBK)	45.81
Talc	15.16
Red Fluorescent Pigment	6.32
Sodium Tripolyphosphate	0.60
MIBK	3.48
M-Pyrol	21.17
Kynar	2.53
Antifoam 66	2 drops
<u>Part B:</u>	
Versamid X 265-WR70	4.42
Butyl Alcohol	0.51

The electrodeposition experiments are summarized in Table VIII.

### 2. Preparation of Epoxy-Based Blue Paint Emulsion

#### Formulation IEB\*

<u>Components</u>	<u>%-by wt.</u>
<u>Part A:</u>	
Epon Resin 1007 (25% in MIBK)	48.09
Talc	15.92
Magnesium Phthalocyanine	1.66
Sodium Tripolyphosphate	0.63
MIBK	3.65
M-Pyrol	22.22
Kynar 201	2.65
Antifoam 66	2 drops
<u>Part B:</u>	
Versamid X 265-WR70	4.64
Butyl Alcohol	0.53

Note: \*EB = Epoxy-based, Blue

### 3. Preparation of Epoxy-Based Yellow Paint Emulsion

#### Formulation IEY\*

<u>Components</u>	<u>% by wt.</u>
<u>Part A:</u>	
Epon Resin 1007 (25% in MIBK)	47.31
Talc	15.66
Yellow Fluorescent Pigment	3.26
Sodium Tripolyphosphate	0.62
MIBK	3.59
M-Pyrol	21.86
Kynar 201	2.61
Antifoam 66	2 drops
<u>Part B:</u>	
Versamid X 265-WR70	4.57
Butyl Alcohol	0.52

Mixing procedures for IER-IVER consisted of ball milling for one hour. Each emulsion was allowed to stand at room temperature to defoam, if foaming occurred. Otherwise, the emulsion was used immediately after ball milling.

For Formulations VER, VIER IEB and IEY, the mixing procedure is the same as IVEW.

### VII. Preparation of Acrylic-Based Electrocoating Emulsions

#### A. Electrocoating with UCAR Latex 891 (Union Carbide acrylic latex)

##### Formulation IAW\*\*

The following dispersions were prepared:

1. 1% dispersion (L) - 2 g. UCAR Latex 891 (49.8% solids) in 100 ml. deionized water

Note: \*EY = Epoxy-based, Yellow

\*\*AW = Acrylic-based, White electrocoating emulsion

2. Pigmented 1% dispersion (PL) - 2 g.  $\text{TiO}_2$ ,  
4 g. UCAR Latex 89. in 200 ml. deionized  
water
3. Conductive 1% dispersion (PCL) - 1 g.  $\text{TiO}_2$ ,  
0.5 g. aluminum powder, 2 g. UCAR Latex 891  
in 100 ml. deionized water.

The dispersions were electrocoated on  
aluminum and fiberglass. The electrodeposition  
parameters and the results are shown in Table IX.

To improve conductivity of nonconductive sub-  
strates, 10% aqueous solution of a quaternary  
ammonium chloride salt (Arquad 16-50) was used for  
sizing of surfaces.

4. PCLK - 1.0 g. Kynar and 20 ml. acetone (to dis-  
perse the Kynar) were added to dispersions 3  
(PCL).

#### Formulation IIAW

<u>Components</u>	<u>% by wt.</u>
Grind:	
Titanium Dioxide	5.01
Acrylic Resin (Goodrich Hycar 2600 x 171)	15.15
Amine (Diethylethanolamine)	enough to adjust pH to 7.05 - 7.10
Deionized $\text{H}_2\text{O}$	10.10
Sodium Hexametaphosphate	0.15
Let Down:	
Acrylic Resin (Goodrich Hycar 2600 x 171)	4.84
Diethylethanolamine	enough to adjust pH to 7.2 - 7.3
Deionized $\text{H}_2\text{O}$	64.90

### Formulation IIIAW

<u>Components</u>	<u>% by wt.</u>
Grind:	
Titanium Dioxide	4.60
Moly White 101	3.06
Talc	4.59
Acrylic Resin (Hycar 2600 x 171)	13.92
Diethylethanolamine	Adjust to pH 7.05 - 7.10
Deionized H <sub>2</sub> O	9.28
Sodium Hexametaphosphate	0.14
Let Down:	
Acrylic Resin (Hycar 2600 x 171)	4.45
Deionized H <sub>2</sub> O	59.95
Diethylethanolamine	Adjust to pH 7.2 - 7.3

The grind components were ball-milled for one hour. The let down components were added slowly with stirring, one component at a time and the mixture ball-milled for another 1/2 hour.

### Formulation IVAW

<u>Components</u>	<u>% by wt.</u>
IR Acrylic Stock Electrocoat	2.24
Emulsion	
Deionized H <sub>2</sub> O	87.21
Sodium Tripolyphosphate	0.72
Talc	8.94
Cerium Acetylacetonate	0.89

The components were ball-milled for four hours or until dispersion appeared complete (no lumps or grains in emulsion).

#### Formulation VAW

<u>Components</u>	<u>% by wt.</u>
IR Stock Acrylic Emulsion	28.57
Deionized H <sub>2</sub> O	71.43

The components were ball-milled for one hour, filtered using a fluted filter paper and the filtrate used for electrodeposition. The filtered emulsion is stable for weeks at room temperature.

#### Formulation VIAW

<u>Components</u>	<u>% by wt.</u>
IR Stock Acrylic Emulsion	71.43
Deionized H <sub>2</sub> O	28.57

#### Formulation VIIAW

<u>Components</u>	<u>% by wt.</u>
IR Stock Acrylic Emulsion	28.57
Kynar Powder	1.0
Deionized H <sub>2</sub> O	70.43

#### Formulation VIIIAW

<u>Components</u>	<u>% by wt.</u>
IR Stock Acrylic Emulsion	28.57
Kynar 202 (44% Kynar in MEK+DMP)	1.00
MEK+DMP	1.27
Deionized H <sub>2</sub> O	69.16

Formulation VIAW - VIIIAW were prepared by weighing out all the components into the ball mill, milling for one hour and filtering before electrodeposition.

MEK - Methyl Ethyl Ketone

DMP - Dimethyl Phthalate

VIII. Preparation of Paint Emulsion based on Acrylic-Epoxy Crosslink

Formulation IAECW\*

<u>Components</u>	<u>% by wt.</u>
Grind:	
Carboset 525 (10% in $\text{NH}_3\text{-H}_2\text{O}$ )	36.49
Deionized $\text{H}_2\text{O}$	9.12
Titanium Dioxide	15.20
Letdown:	
Carboset 525 (10% in $\text{NH}_3\text{-H}_2\text{O}$ )	24.33
Deionized $\text{H}_2\text{O}$	9.12
D.E.R. <sup>®</sup> 332 Epoxy Resin	4.99
EH 330	0.75

Note: 10% Carboset 525 was prepared by dissolving 10 g. Carboset 525 in 88.8 g. deionized  $\text{H}_2\text{O}$  + 1.2 g. concentrated  $\text{NH}_4\text{OH}$ .

The grind portion was mixed in a colloid mill for one hour. Simultaneously, the letdown portion was mixed with a magnetic stirrer in a glass vessel. The letdown portion was gradually added to the grind portion, stirring between additions, and allowed to stand overnight to defoam.

Formulation IIAECW

<u>Components</u>	<u>% by wt.</u>
Grind:	
Carboset 514 H (40% solids)	36.30
Deionized $\text{H}_2\text{O}$	9.06
Titanium Dioxide	15.13
Cobratec TT-100	0.15
Kynar	0.12
Octyl Alcohol	0.12

Note: \*AECW = White Acrylic-Epoxy crosslink-based paint



Letdown:

Carboset 514 H	24.20
Deionized H <sub>2</sub> O	9.08
D.E.R.® 332 Epoxy Resin	4.96
EH 330	0.75
Octyl Alcohol	0.12

Formulation IIIAECW

<u>Components</u>	<u>% by wt.</u>
Grind:	
Carboset 514 H	32.71
Deionized H <sub>2</sub> O	8.18
Titanium Dioxide	13.63
Cobratec TT-100	0.13
Kynar	10.00
Octyl Alcohol	0.11

Letdown:

Carboset 514 H	21.81
Deionized H <sub>2</sub> O	8.18
D.E.R.® 332 Epoxy Resin	4.47
EH 330	0.68
Octyl Alcohol	0.11

Formulation IVAECW

<u>Components</u>	<u>% by wt.</u>
Grind:	
Carboset 514 H	34.43
Deionized H <sub>2</sub> O	8.61
Titanium Dioxide	14.35
Cobratec TT-100	0.14
Kynar 301-F	5.27
Octyl Alcohol	0.11

Letdown:

Carboset 514 H	22.95
Deionized H <sub>2</sub> O	8.61
D.E.R. <sup>®</sup> 332 Epoxy Resin	4.71
EH 330	0.71
Octyl Alcohol	0.11

Dispersion Procedure for IIAECW - IVAECW

The grind components were weighed into the colloid mill and stirred for one hour. The letdown components were then added, one component at a time, with agitation. When all the letdown components had been added, the mixture was milled for another half-hour. The paint emulsion was allowed to stand for a few hours to overnight to defoam.

IX. Preparation of Acrylic Paints for Silk Screening

A. White Silk Screen Paint

<u>Components</u>	<u>% by wt.</u>
IR Acrylic Stock Emulsion	55.01
Titanium Dioxide	26.87
Natrosol 250 MR (5% in H <sub>2</sub> O)	15.29
Ethylene Glycol	2.01
Kynar	0.83

B. Blue Silk Screen Paint

<u>Components</u>	<u>% by wt.</u>
IR Acrylic Stock Emulsion	45.60
Magnesium Phthalocyanine	5.47
Titanium Dioxide	28.18
Ethylene Glycol	1.69
Natrosol 250 R (5% in H <sub>2</sub> O)	18.38
Kynar	0.68

The silk screen paints were mixed using the Virtis homogenizer for 10-20 minutes until the emulsions appeared completely homogeneous.

## DISCUSSION OF RESULTS

### Autocatalytic Reduction Copper

The art of electroplating plastics is the conversion of nonconducting polymers into a form capable of attracting charged ions from an electrolyzing solution. Three principal stages are involved:

- a. Preparation of the surface of the plastic to receive a conductive coating
- b. Application of conductive layer
- c. Electroplating

Out work in this project to render the FX-resin impregnated fiberglass capable of accepting the electrocoating included stages a. and b., the pretreatment cycles. Essentially, the objective was to provide the fiberglass surface with a smooth adherent coating of copper on which electrodeposition can subsequently be made.

The procedure is outlined in Figure I. Electroless plating is an autocatalytic reduction deposition process which means that reduction has to be initiated by a metal such as palladium, silver, gold, etc. Once the metal (copper or Ni) starts depositing, it catalyzes the reduction allowing a considerable thickness of metal to be deposited.

In the solvent bath, the sample was rendered water-wettable and "satinized". It should be pointed out that plastic surfaces are hydrophobic. It is essential to make the surface water-wettable so that subsequent chemical reaction can take place. The perchloroethylene degreased, cleaned and roughened the surface of the FX-resin impregnated fiberglass. Heating promoted completion of the chemical reaction. These steps produced anchorage points that were uniformly distributed on the surface. The rinsing step removed excess chemicals from the surface. Thorough rinsing is important to assure success in the plating operation.

The chemical etching further roughened the surface. The etchant should only attack the surface because penetration of the bulk of the material results in embrittlement. The potassium hydroxide etching proved sufficient for most of the samples. The phosphoric acid etching was used only when the desired roughening was not attained after 3 minutes in the caustic potash solution.

Rinsing was done 2-3 times to assure complete removal of the etchant.

Sensitizing aided in the deposition of the metal film. Tin II salts readily form organometallic complexes and maybe this is the mechanism by which the Sn(II) bonds with the plastic surface. This is a weak bond, though, and the use of the milky rinse after sensitizing was to produce a controlled hydrolysis of the Sn (II). The hydrated stannous (chloride) complex is more polar and should adhere to the plastic surface better.

The clean rinse removed any excess Sn salts and prevented contamination of the activating solution.

The activating step was to lay a thin film of silver on the surface to accelerate the chemical plating. When the sensitized material was immersed in the activating bath, an exchange reaction occurred. The sensitizing divalent tin ions were oxidized to the tetravalent state while the Ag (I) was reduced to the metallic state forming a thin metallic film.

Rinsing is extremely important after the activating step. A trace of Ag metal carried over to the plating step will cause premature precipitation in the chemical plating bath. The reduction is autocatalytic and can only be stopped by filtering off the precipitate. The rinsing was done with running water followed by spray rinsing for assurance that all the holes and recesses in which excess silver metal may have been trapped has been reached.

The chemical plating solution was a modified Fehlings solution. Copper sulfate was the source of the metal. Complexing agents (solution stabilizers) were sodium potassium tartrate and tetrasodium ethylene diaminetetraacetic acid. The sodium hydroxide was used to adjust the pH between 11-12.5 (working range) and the sodium carbonate acted as the buffer increasing the solution stability. The formaldehyde was the reducing agent to start the auto-catalytic reduction copper plating. Our laboratory experience showed that the best copper deposit (uniformity and thickness) was obtained by adding the formaldehyde after the material to be plated has been immersed in copper solution (Part A) of the plating solution. Only 20% of the formaldehyde was added at one time to control the thickness of the deposit and prevent "wild" deposits of copper on the sides of the plating bath. The material being plated was lifted from the solution every five minutes to examine for uniformity. When the deposit got too thick, the copper coating became uneven and the surface took on a coarse appearance.

Resistance measurements ranged from 10 ohms to 1 K ohm. Dull surfaces had low resistance, in the order of 10 ohms. Most shiny surfaces had resistance in the order of 40 ohms. A few pieces gave as high as 1 K ohm. All these pieces were electrically conductive enough for our electrodeposition experiments. The kind of copper deposit in the final plating step that the surface would show was not predictable because of the lengthy history of pretreatment steps. Care was exercised to subject all the samples to as uniform a treatment as possible.

#### Electrodeposition with Polyvinylidene Fluoride (Kynar)

One of the initial objectives in the research program was to render the FX-resin-impregnated fiberglass (FRIF) white.

Polyvinylidene fluoride (Kynar) is white; therefore, attempts were made to electrodeposit Kynar on the copper-plated FRIF. The Kynar was deposited by application of 200 volts and 300 volts for three minutes each. In both cases, white, thick and uniform coatings were obtained. The coatings were not adhesive enough without heat curing. On curing at 325°F, followed by heating to 525°F, the white coating became transparent and very adhesive. These experiments indicated that Kynar alone would not produce the white color desired.

The next approach taken was to attempt to produce a white and conductive resin formulation that could be incorporated with fiberglass and subsequently pressed and baked into sheets. The results are shown in Table I. The FX-resin is so strongly colored (dark brown) that efforts to hide the color with different white pigments were fruitless. The colors varied from grayish-white to brownish pink. Conductivity could be imparted by incorporation of metal powder but the degree of resultant conductivity was not predictable. This is due to the fact that the resin encapsulates the metal insulating the electrical conductivity. Only the presence of free metal adhering on the resin surface makes the substrate effectively electrically conductive. For assurance that enough free metal atoms will be present on the surface, the formulation should have a large amount of the metal which renders the formulation economically unpractical. The excessive quantity of metal would also impart some undesirable properties such as added weight, brittleness, color other than white, etc.

A homogenized formulation of the FX-resin with about 2% atomized aluminum was used to coat fiberglass mat. The surface of the coated sheet gave uneven resistance measurement so that subsequent electrodeposition produced uneven coatings.

Five and 10% metal-containing formulations produced the same results.

#### Considerations in Formulation of Electrocoating

The electrocoating desired must produce coatings that are decorative, protective (abrasion-resistant, corrosion-resistant, stain-resistant and temperature stable) and easily cleaned. The application method of choice is electrodeposition because of the advantages of the method:

- a. Economy - low operating cost, ease of automation, speed of coating.
- b. Quality - uniform pin-hole coating, coatings on recessed areas, superior adhesion and corrosion resistance because the uniform dense film is forced against the substrate during plating.
- c. Selectivity - only electrically conductive areas are coated allowing ease of design application.
- d. Versatility - odd shapes can be uniformly coated; by proper choice of components and baths, different properties can be obtained.

For electrodeposition, the coating must consist of charged particles suspended in a medium capable of conducting electrical charge. These charged particles are colloidal suspensions of pigments in organic film-forming macroions known in the coatings industry as resins. These film formers may be acidic resins, functionally described as  $R(COOH)_n$  or alkaline resins,  $R NH_2$ , where the R has molecular weight ranging from 5000 - 50,000 and equivalent weights of 100 - 2000.

In electrocoating, three electrolytic processes take place when the potential is applied:

- a. Electrolysis - the paint separates into negatively charged paint solids and positively charged solubilizing agents
- b. Electrophoresis - the negatively charged paint particles move to the anode and deposits on it
- c. Electro-osmosis - movement of water and soluble components out of the film

When the conductive surface has been coated, the dipped anode becomes coated with an additional film of adhering paint called "dragout". This can be rinsed off or allowed to drip.

For electrocoating metals, total paint solids of 10-15% are sufficient. In our work, some of our formulations have higher percentage of paint solids. The reason is that conductivity induced by pretreatment of the nonconductive substrate is very small relative to that present in metals. The presence of more solids allow more charges to move in the electrochemical cell and increase the plating efficiency.

In electrocoating systems, the vehicle or binder exerts more influence on the performance of the pigmented electrocoat system than the pigment itself. The quality of the deposited film is dependent on the molecular weight of the vehicle. The higher the molecular weight, the better is the cohesion or toughness, adhesion, solvent resistance and high temperature resistance. In our investigation, we limited our choice of vehicles to high molecular weight polymers.

Two polyvinyl polymers were tried as carriers. Polyvinylidene chloride is a thermoplastic polymer of vinylidene chloride (1,1-dichlorethylene). Daran 211, a 60% polyvinylidene chloride emulsion from Grace Organic Chemicals, was incorporated into our formulation. Daran coatings are high



barrier coatings, particularly good for penetration resistance to water, moisture and oxygen.

Two polyvinylidene chloride-based formulations were prepared, the difference being in the pigment content. Too much current was developed during electrodeposition with the first formulation which contained 15% titanium dioxide. In the second formulation, 5% Moly White 101 from Sherwin Williams was substituted for some of the titanium dioxide. Moly White is a basic zinc molybdate compound and its incorporation lowered the total current developed during the electrodeposition.

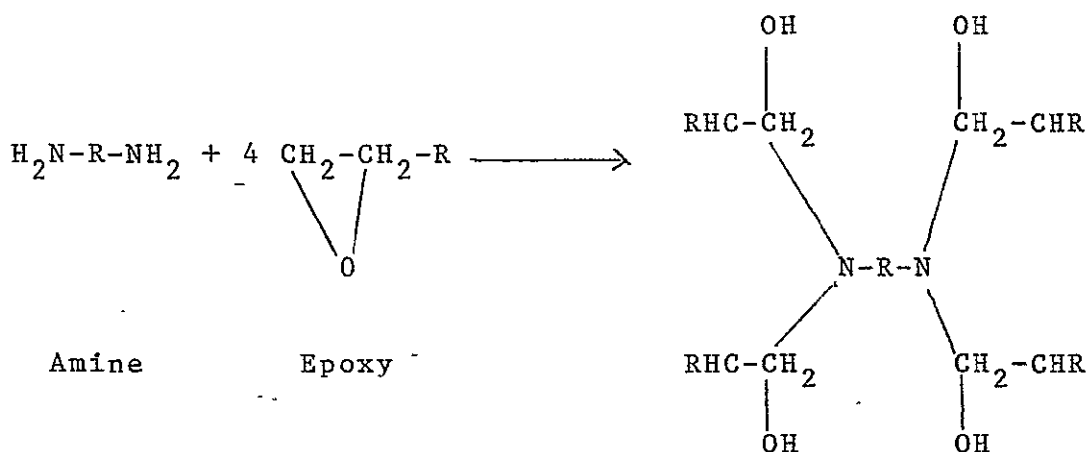
Polyvinyl acetate is a thermoplastic material consisting of polymers of a vinyl acetate. Vinac 880 was used which is a low viscosity aqueous dispersion with about 48% homopolymer. In this formulation, sodium tripolyphosphate was used to disperse the titanium dioxide. Sodium tripolyphosphate is an anionic surfactant and acts by imparting negative charges on the pigment. Dispersion is due to repulsion of like charges. Lecithin aided in the dispersion of titanium dioxide. In addition, it helped in viscosity control to improve the flow and levelling properties. Dichloroethane and tributyl phosphate were for flame retardancy.

The results summarized in Table II show that the polyvinyl-based paint emulsions were readily deposited at low voltage. The coatings could be heated only to 500°F. Above 500°F, charring occurred.

Aluminum was used as the substrate in most of the experiments. For preliminary tests, aluminum anodes were employed to diminish the number of undefined variables. Use of aluminum assures the presence of a complete electrical path for electrodeposition.

Epoxy-based coatings are known for their toughness, hardness (abrasion-resistance) and flexibility. Temperature resistance increases with the molecular weight.

Epoxy resins are thermosetting resins containing the epoxy group. The properties imparted to the paint film are not solely from the epoxy but rather are results of the reaction of the epoxy with other materials through the terminal epoxide, secondary hydroxyl or both types of groups in the molecular structure. The curing materials may be an amine, a polyamide, amine adducts, ketimines, etc. A three-dimensional crosslinked product appears in the cured film, such as follows:



Three Dimensional Crosslinked  
Cured Product

The quality of the cured film is affected by the quantity of curing agent added. Too much curing agent, as well as too little, results in a looser degree of crosslinking and poorly cured films. The stoichiometric amount of curing agent (the amount needed to provide one amine hydrogen per epoxide group in the resin) can be calculated from:

$$\text{stoichiometric amount (phr)} = \frac{\text{equivalent weight of amine} \times 100}{\text{epoxide equivalent of resin}}$$

phr - parts by weight of amine per 100 parts by weight of epoxy resin

where:

$$\text{equivalent weight of amine} = \frac{\text{molecular weight of amine}}{\text{number of amine hydrogens}}$$

epoxide equivalent of resin = grams of resin containing one gram - equivalent of epoxide

Several epoxy-based electrocoatings were formulated and evaluated in our laboratory. Formulations IEW - VEW had epoxy dispersed in an organic solvent. In IEW, IIEW and VEW formulations, the epoxy used had an epoxide equivalent of 2000 - 2500 while in IIIEW and IVEW, the epoxy had an epoxide equivalent of 193 - 204. Silica-free, extra-fine titanium dioxide was used in pigmentation for ease of dispersion. Pigmentation with Moly White 101 was to decrease the current developed in plating. The mechanism of reaction was not determined in this study but it is conceivable that its basic nature raises the pH sufficiently to alter the kinetic rates of the different reactions taking place during electrodeposition resulting in the overall decrease in current.

For extender, extra-fine talc powder was used. Sodium tripolyphosphate was for pigment dispersion. Kynar powder was incorporated to add non-abrasive and stain-resistant properties. Methyl isobutyl ketone was used to dissolve the epoxy. M-Pyrol was chosen as diluent because of its ease and safety in handling and its compatibility with the system. For curing agent, ethylamine was used in the first formulation but was replaced with a polyamide in subsequent formulations because of some undesirable properties (difficulty in handling, unpleasant odor and toxic properties). Butyl alcohol and G.E. silicone antifoam agents were added to diminish foaming during the milling or homogenizing step.

Formulation IVEW is a modification of IIIEW by addition of different intumescent agents. VEW was an attempt to produce a conductive coating by addition of aluminum flakes to IIIEW. A grayish-white paint was obtained. On electrodeposition and drying, the film did not exhibit conductivity. Whatever aluminum was attracted to the anode was encapsulated in the paint. The free aluminum ions did not deposit on the anode because of its positive charges.

The experiments with IEW are given in Tables III and IV. A good coating was obtained with aluminum but not with the copper-plated FX-resin impregnated fiberglass. The rate of electrodeposition at constant voltage was found to be directly proportional to the time (Table IV) which indicates that the thickness of coating can be controlled once the optimum voltage requirement has been determined. Good agreement was found between duplicate experiments. Preliminary experiments on coating Kynar over the paint was performed. The deposition of the film of paint on the aluminum and on the copper-plated fiberglass resulted in making the surface essen-

tially insulated and nonconductive. Attempts to coat with Kynar resulted in deposits only wherever cracks were found. Electrical conductivity was induced by using a metal backplate.

#### Induction of Electrical Conductivity by the Frame Technique

Our method of inducing conductivity is based on a simple phenomenon: As the colloidal paint particles are attracted to the anode under the influence of applied potential, a nonconductive surface placed in between acts as a sieve or a barrier. The porosity of the barrier and the size of the colloidal particles determine if electrodeposition will take place. If the barrier is porous enough (i.e., colloidal particles are smaller than the pores), the paint particles will filter through and deposit on the metal anode. If the barrier is dense enough, the paint particles will deposit on it. The strength of adhesion of the film to the barrier is defined by surface conditions. The principle is illustrated in Figure III. The anode configuration is shown in Figure IV. It consists of a nylon front plate with a window as big as the substrate to be coated, the nonconductive substrate, an aluminum backplate and a solid nylon plate. Screws or metallic clamps were used to hold the four pieces together. The aluminum backplate is slightly longer than the nylon frame to allow clamping of the electrode. The solid nylon plate behind the aluminum prevents coating on the back side of the aluminum. This allows use of the aluminum over and over, providing that no deposition occurs on the front side.

A major advantage of this method is that electrocoating can be done on a surface several times. Normally, a surface

can only be electrocoated once. The film insulates all the electrical properties of the substrate.

The substitution of a polyamide (General Mills Versamid X 265-WR70) for the ethylamine was made not only for the undesirable properties of ethylamine but also to get a better, easily electrodeposited and more adherent coating. A lot more foaming occurred indicating a difference in the rates of reaction in the curing of the epoxy. This polyamide is of proprietary nature and the exact composition unknown. It is possible that there are components in the polyamide dispersion that reacts with the paint components causing a lot of gassing. The formulation had to be stored in the refrigerator to defoam. The addition of a few more drops of antifoam agent decreased the foaming. The addition of much antifoam agent is not recommended because it diminishes adhesion properties of the paint. The experiments with IIEW are shown in Table V. The application of 125 volts across the electrodes did not deposit the paint on the nonconductive resin-impregnated fiberglass (FRIF). No electrodeposition took place with the frame and with aluminum alone. This indicates that the voltage is not high enough to force the movement of the charged paint particles to the anode. By doubling the voltage and increasing the time, electrodeposition was effected, the rate of deposition being  $0.3 \text{ g/in}^2$  in two minutes. The coating was not very stable on heating, turning yellow after ten minutes at  $350^\circ\text{F}$ .

One drawback of epoxy-based paints is the limited pot life after addition of curing agent. The above formulations had pot life of about 48 hours at room temperature and about 3-4 days when refrigerated. Time of formulations is long because of the difficulty in dissolving the Epon Resin 1007

in the ketone solvent. Epon Resin 829 was substituted in the formulation. The latter is a liquid and its use facilitated faster formulation of the paint.

Coating of formulation III EW (containing Epon Resin 829) on the nonconductive substrate was done at 250 volts for periods ranging from 60 to 120 seconds. It should be mentioned that a bigger current developed in the electrodeposition bath with the liquid epoxy resin. Thin uniform coatings were obtained which turned yellowish when cured at 325°F for 30 minutes. At 375°F, the coatings turned brownish. Intumescent agents were added to promote temperature stability (Formulation IV EW). The results of the experiments are given in Table VI. The presence of the intumescent agents increased the temperature stability to 400°F. Overcoating with Kynar also improved heat stability. The thicker the coating (c), the more yellowing was observed on heating.

In our search for improvement in our electrocoatings, a shift to a water-reducible epoxy vehicle was made. By esterification of the epoxy, free carboxyl groups are introduced which can react with an amine to form a water-soluble salt. A proprietary scheme was adapted with a few modifications to esterify the epoxy resin.

Bisphenol A and linseed oil fatty acids were added to Epon Resin 829, a precatalyzed liquid epoxy resin to prepare higher molecular weight resin esters with short oil length chain. Benzoic acid was substituted for the wood resin to get harder film. Stannous octoate catalyzed the esterification reaction. The maleinization step after the complete esterification of the epoxy resin incorporated free carboxyl groups. The ester mixture was highly viscous and was thinned to about 80% solids content with a water-miscible organic solvent such as methyl oxitol.

In the preparation of the pigment concentrate, an ethoxylated fatty amine was used to aid in pigment dispersion into the water-reducible esterified epoxy. Benzylamine was used for curing. The complete esterification of the epoxy was not attained, which was indicated by incomplete dispersion in deionized water in the final dilution step to 10% solids. A probable cause is that the mixture did not attain and maintain the temperature during the esterification process. Instead of using deionized H<sub>2</sub>O, a mixture of methyl oxitol, acetone and water was used for dilution.

Electrodeposition at 250 volts produced too much current since the potential could only be applied for 10-15 seconds without blowing a fuse. The coatings were thin and uneven. Even at 150 volts, the current developed was still high. Electrodeposition was limited to very short times and coatings obtained were thin and uneven.

Another water-reducible epoxy electrocoating emulsion was prepared using an epoxy ester proprietary formulation (VIEW).

Natrosol 250 HR, a water-soluble hydroxyethyl ether of cellulose, was added as a protective colloid dispersant, and as a viscosity control agent. Tween 20 was used as an anionic surfactant and found to aid in pigment dispersion and emulsion stabilization. The Aurasperse W4123 is a phthalocyanine pigment and was added to improve the whiteness and hiding property of the emulsion.

The experiments with this formulation (VIEW) are summarized in Table VII. The paint emulsion deposited evenly on the FX-resin impregnated fiberglass (FRIF), both with metal-coated surface and with the inductively charged surface (frame method). It is interesting to note that the coating on the copper-plated



FRIF is more white than the coating on the plain nonmetallic surface. The dark reddish brown color of the FX-resin on the fiberglass caused an off-white color of the coating. By recoating, effectively producing a thicker coating, the brown color was completely obscured and the electrodeposited coating appeared more white.

4" x 5" pieces of the FRIF were coated with formulation VII EW, then silk-screened (at NASA) with different colored symbols. The silk screened pieces were overcoated with 1% Kynar at 100 volts for one minute. One was cut up into 4 parts and temperature resistance tests were run. The test consisted of heating at 400°F, 450°F and 500°F for 10 minutes. The heating at 400°F caused slight yellowing of the coating. At 450°F, the change in color (yellowing) was not significant from that at 400°F. Heating at 500°F turned the coating brown.

Formulation VII EW was easily depositable on the fiberglass wherein even coatings were produced. High currents developed during electrodeposition requiring the use of 3-4 power supplies connected in parallel. This epoxy coating was very adhesive and tough. The only disadvantage is that the coating can not be heated to very high temperatures without darkening.

Studies were also made on pigmentation of epoxy-based paints. Red was a difficult color to obtain. In most of the formulations, the emulsion looked red but on electrodeposition, the coating ranged from yellow to reddish brown. A possible explanation is incomplete dispersion of the pigment. On electrodeposition, the pigment settled to the bottom. A red fluorescent pigment from Americhem was compatible with the epoxy formulation and found to give even melon red coating.

Blue and yellow electrocoatings were also prepared and electrodeposited on FX-resin impregnated fiberglass (FRIF)

that has been electrocoated with white paint emulsion (white FRIF).

Stripes of red, blue and yellow were painted on white FRIF, dried at room temperature or at 150°F. The brushed-on coats were very tough. Kynar was overcoated electrophoretically using the frame method. The Kynar deposits were uneven. The Kynar could not be cured properly (at least 325°F for 30 minutes, shorter time at higher temperature) because the coatings turn brownish on heating.

Acrylic-type emulsions are noted for their temperature and heat stability. Acrylic formulations were evaluated with several substrates. A 1% aqueous dispersion of an acrylic latex gave even, smooth coating on aluminum but very thin and uneven coating on FRIF by the frame method. The aluminum backplate was coated evenly. Pigmenting with titanium dioxide or aluminum powder did not improve the quality of the electrodeposit on the FRIF. The aluminum flaked out of the dispersion with the application of voltage. This indicated that the aluminum was not colloidally dispersed. Electrodeposition with the FRIF alone as anode hardly gave a deposit. A thin coating which became bubbly on heating was deposited on the copper-plated FRIF. These experiments indicate that the FRIF is too porous relative to the size of the acrylic-dispersed paint particles. The copper ions on the surface served two roles. Aside from providing electrical conductivity, it decreased the porosity of the substrate so that electrodeposition could take place.

The conductive fiberglass coupons (impregnated with FX-resin and aluminum) prepared in our laboratory were coated unevenly. With the same electrodeposition parameters, some pieces were coated thickly and some very thinly. Raising the

voltage over 200 volts caused smoking of the anode and still uneven deposition. This was explained by the non-uniform dispersion of aluminum due to colloidal entrapment of the metal atoms.

Another acrylic-based emulsion was prepared by dispersing titanium dioxide in 50% acrylic resin solution from Goodrich Chemical Company (Hycar 2600 x 171). Hycar 2600 x 171 was found to have excellent resistance to discoloration from heat and light aging. Its soft and elastic property helps offset the stiffening effect of pigments and additives. Sodium hexametaphosphate was incorporated for added gloss. Diethylethanolamine was used to raise the pH to the basic range which is suitable for anodic electrodeposition.

Electrodeposition at 100 volts for ten seconds produced a thick, bubbly deposit on aluminum and a very thin coating on the FRIF by the frame method. A current surge to about 450 ma was observed on application of potential. A rapid exponential decay of current to about 50 ma occurred with 15 seconds.

The thin coating on the plastic surface indicated the need for a more viscous emulsion. Talc was added as a filler in one formulation. Moly White was also incorporated to lower the current in the system. A longer milling time (1-1/2 hours) was allowed to get a good dispersion and overnight standing to defoam. Electrodeposition on the fiberglass and on aluminum indicated that the acrylic-pigment colloids filtered through the FRIF. The formulation exhibited instability to repeated passage of current. After six electrodeposition experiments, settling occurred. This problem was remedied by addition of protective colloids such as Natrosol. Curing of the coatings proved to be difficult. Heating to 450°F

for one hour was not sufficient to dry the coating. However, no discoloration occurred which demonstrated the temperature stability of the acrylic-based system.

A proprietary acrylic concentrate was evaluated. Initial experiments were made to find a suitable dilution ratio, pigmentation, and dispersing agent. Early results indicated that dilute solutions (2.5% acrylic) gave nonuniform coatings. Thickness could be varied by increasing the time of application of voltage. The coating on FRIF was thin and uneven and could be washed off with water before curing. Sizing with Arquad 16-50 (a quaternary ammonium salt) enhanced the current development but not the quality of the paint film. A 10% pigment could not be dispersed even with addition of surfactant (sodium tripolyphosphate) and milling for four hours.

A 10:1 acrylic electrocoat stock solution: water dilution (91% acrylic) gave very high currents (over 500 ma at 200 volts). Thick smooth coatings were obtained on aluminum which bubbled and dripped on curing at 350°F. The acrylic system cured in 5-10 minutes at 350°F. Coatings on the FRIF were also even and thick. Bubbling also occurred on heating at 350°F indicating that a 10:1 acrylic: H<sub>2</sub>O formulation was too concentrated. Bubbling was found to result from the "drag" which is defined as excess paint deposit.

A more dilute dispersion, 2.5:1 acrylic:H<sub>2</sub>O (71.4% acrylic) was prepared (Formulation VIAW). The electrodeposition experiments are summarized in Table XI. The deposits were thin and uneven on the fiberglass while the aluminum backplate received a thick coating. Sizing by brushing a solution of quaternary ammonium salt on the surface appeared to have plugged the pores and improved the electrical conductivity of the surface. The deposits were thick and even. There was so much "drag"

that bubbly coatings were obtained on heating.

A 1:1 acrylic:H<sub>2</sub>O dilution (50% acrylic) gave thin, uneven electrodeposits on both the unsized and sized non-conductive FX-resin impregnated fiberglass.

Kynar was incorporated in the next formulations not only to improve the properties of the cured film but also to act as a filler (to effect increase in the size of the colloidal paint particles). Formulation VIIAW and VIII AW both had 1% Kynar incorporated in the form of a pasty emulsion in organic solvents. The pasty emulsion was easier to homogenize with the acrylic. The amount of the acrylic was also decreased to 28.6% to lower the currents during electrodeposition.

Studies were conducted on aluminum to determine optimum electrodeposition parameters for this dilution ratio. The results showed that constant stirring of the bath promoted a more uniform film deposit. Washing with deionized water to remove the drag improved uniformity of the coating but decreased the gloss. Longer curing (from 5 minutes to 10 minutes) did not affect the gloss. The thicker the coating, the more glossy the coating was.

For aluminum, the best deposit (uniformity, gloss, thickness) was at 150 volts for 90 seconds. The rate of deposit was 8.9 g/cm<sup>2</sup>. The solution was very stable. After one week standing at room temperature, the quality of the coatings obtained remained the same.

Electrodeposition on FX-resin impregnated fiberglass in the frame produced very thin and uneven coatings. Obviously, the fiberglass is too porous for the acrylic emulsion. Pieces of the fiberglass were copper-plated to plug the pores and to impart electrical conductivity.

Electrodeposition at 150 volts and 200 volts for 1-3 minutes produced thin and even coatings. Thicker coatings were obtained by using the frame technique. However, the coatings had a greenish tint. The copper and the acrylic underwent a complexation reaction (corrosion) to give the green color.

At this point, several substrates were tried for compatibility with the acrylic. Electrodeposition experiments were conducted on polyether sulfone, polyphenylene sulfide and a unidirectional fiberglass impregnated with polyimide. These substrates have very smooth surfaces in contrast to the matted finish of the FX-resin impregnated fiberglass.

Initial electrodeposition using the frame method showed that the acrylic coated on these substrates but the adhesion was so poor that on curing with the substrate held vertically in the oven, the acrylic dripped leaving very thin, uneven but tenacious coatings. The poor adhesion prior to heating is due to the smoothness of the surface. Curing in a vertical position did leave more coating but the coatings were uneven and bubbly.

To produce anchorage points on the surfaces of these substrates, electroless copper plating was done. The initial thought about the green tint of the acrylic on the FRIF was a complex involving the FX resin, the copper and the acrylic.

Solvent treatment was different for these substrates. The solvent used has to be a poor solvent for the substrate such that swelling occurs without chemically changing the resin structure. Polyether sulfone was initially stress-relieved by heating for 12 hours at 165°C. (329°F.) and then immersed in dimethyl formamide for a few minutes to swell. The heating prevents cracking in the subsequent stages of treatment. The polyphenylene sulfide and the polyimide-impregnated fiberglass

were swelled in chloroform and in dimethyl formamide, respectively.

For etching, an acidic solution containing 0.5% potassium dichromate was used. The rest of the copper plating process was the same as that described earlier in this report.

Electrocoating the copper-plated substrates with acrylic gave smooth, even, greenish-white coatings. It was observed that the thicker the copper film, the more green was the coating, indicating that the complexation involved only the copper layer and not the resin in the substrate.

Nickel plating was attempted on all the substrates. The procedure is essentially the same as in copper plating except that in activating, a palladium salt solution was used instead of a silver activating solution. The nickel chloride plating solution contained sodium hypophosphite as reducing agent. Nickel could not be plated on the FX-resin impregnated fiberglass, the polyether sulfone, the polyphenylene sulfide and the polyimide-impregnated fiberglass, even at elevated temperatures.

A piece of polyphenylene sulfide (PPS) was rendered conductive with carbon. The carbon could not be laid down evenly on the surface because of the inavailability of the right mixer and press. Electrocoating with acrylic gave uneven white coatings. Carbon coating under vacuum produced a more even carbon layer and hence more even although thin acrylic coating. For economic reasons, vacuum coating to impart conductivity was discontinued. It is suggested, however, that carbon coating of plastic surfaces for electrodeposition of acrylic paints is a possible route.

To take advantage of the ease of electrodepositing epoxy and the temperature stability of the acrylic, formulations

were prepared where the epoxy and the acrylic were cross-linked. The crosslink could be deposited at lower voltage using the frame method and is stable up to 500°F. The copper corrosion problem was solved by the incorporation of very small quantities of tolyltriazole (0.13-0.15%). Kynar was added in different proportions to determine the minimum requirement for stain resistance. The results are summarized in Table XII. 10% Kynar imparted the stain resistance property desired so that a second overcoat was not necessary. 5% Kynar improved the stain resistance so that a very slight discoloration occurred on standing with mustard.

Conductive coatings (solutions of quaternary ammonium salts in water and in organic solvents) were used in sizing the nonconductive surfaces of the substrates (FX-resin impregnated fiberglass, polyphenylene sulfide, polyimide-impregnated fiberglass and polyether sulfone). Electrodeposition of Formulation AECIVW was done on the sized substrates at 100 and 150 volts for 15-60 seconds. The sized substrates were used as anode in the electrochemical cell with or without the frame and coatings were compared for appearance and thickness.

The paint emulsion electrodeposited easily on the sized substrate without the frame. Thin, smooth coatings were obtained. With the frame, thicker coatings could be obtained under the same electrodeposition conditions. For comparable coatings, the framed sized surface should be coated 50 volts lower and half the time used for coating without the frame. For example, for a 6 mil coating on polyimide surface, the electrodeposition was done at 150 volts for 60 seconds without the frame and at 100 volts for 30 seconds with the frame.

The stain resistance property was the most difficult to achieve. In our investigation, the approach taken was to over-



coat with a thin film of Kynar if the coating with incorporated Kynar was not stain resistant. It was observed that incorporation of Kynar decreased the gloss of the coating (9% loss in transmittance for 10% Kynar). Overcoating with Kynar further lowered the transmittance. This is desirable for a coating with a dull satin finish. The overcoating involved three major problems:

1. The paints on the surfaces to be electrocoated provided a thick insulating barrier.
2. Kynar has limited solubility in a few organic solvents. The electrocoated paints are soluble in most of the Kynar solvents.
3. Proper curing of Kynar to achieve good adhesion and protective properties require high temperature (525°F) which cause yellowing of the electrocoated paints.

The frame method circumvented the first problem in most cases. By studying the kinetic rates of solution of the paints in the Kynar solvent and adjusting the electrodeposition parameters for the Kynar overcoat, successful Kynar overcoating was achieved in some cases. For example, the silk screen inks used at NASA are soluble in methyl isobutyl ketone. When painted on FX-resin-impregnated fiberglass and dried at 310°F for 15 minutes, the solubility is very slight in five minutes. Noticeable leaching (color imparted to methyl isobutyl ketone and loss of weight of painted FRIF) occurs after five minutes. By electrodepositing Kynar in 1-2 minutes, the overcoating was achieved.

Several pieces of FRIF electrophoretically rendered white with an epoxy formulation were silk-screened with red, blue and green silk screen inks. These pieces were overcoated

with Kynar for one-minute duration. It was noted that leaching or swelling of the silk screen paints occurred with the pieces that were not dried completely in the oven. The epoxy coating was stable. In all cases, decrease in gloss was noted.

Although the acrylic coatings and the epoxy coatings were relatively stable to ketone solvents, the crosslink-based coatings were very sensitive to ketones and to a lot of organic solvents as shown in Table XIII. Only diethylene glycol was compatible with the two coatings. However, on heating to 350°F, the diethylene glycol turned brown. Fortunately, incorporation of 10% Kynar in the crosslink-based coatings gave the desired stain resistance. However, investigation is continuing to find the proper solvent for Kynar overcoating of the acrylic-epoxy crosslink-based coatings.

The problem of curing Kynar was encountered with the epoxy-based paints which turned brownish above 400°F. By depositing a thin film of Kynar (repeat electrocoating for thicker films\*), curing can be done from 325°F (30 minutes) to 375°F (15 minutes). The Kynar overcoat raised the temperature resistance of the epoxy coatings so that less yellowish or browning occurred at 400°F. With acrylic-based coatings, curing of the Kynar film was not a problem. The acrylic was found to be stable to 525°F, the desirable curing temperature of Kynar.

\*Repeated electrodeposition of Kynar was done on polyimide-coated fiberglass from Deco to get a range of thickness from 0.07-0.59 mil. using a 1% solution of Kynar.

A pure acrylic system was specifically developed to coat large 4' x 4' polyimide panels. Two 4' x 4' panels of polyimide-impregnated fiberglass were pretreated with the conductive coatings and coated with the preferred coating material using a high surface charge density. An aluminum sheet was used to induce the charge. The amount of Kynar was varied from 10 to 20% for increased protective qualities. Both sides of the panels were coated with varying concentrations of the electrocoating material. One side was overcoated with Kynar for comparison of appearance and properties. The curing was done at 400°-425°F in a circulating air oven for 30 minutes. Extremely adherent decorative coatings were obtained. Samples of the coated polyimide and phenolic are presented as part of the final presentation.

The physical properties are summarized in Table XIV. The thermogravimetric analyses results are shown in Figures V to XIII. Figures VI, VIII, X and XII show the different coatings with added Kynar. Figures VII, IX, XI and XIII are for the different coatings without the Kynar. Figure V is for the Kynar alone. The thermogravimetric analyses demonstrate that Kynar shifts the decomposition temperature and lowers the weight loss of the coatings.

## SUMMARY

Our investigation has shown that nonconductive materials may be electrocoated satisfactorily by the IR electrophoretic process. Sizing with quaternary ammonium salts and/or application of a metal frame provided enough electrostatic charge so that the nonmetallic surface became receptive to accepting electrically charged paint particles. The FX-resin-impregnated fiberglass and the polyimide-impregnated fiberglass were coated successfully with an acrylic-type paint containing polyvinylidene fluoride is recommended. This type of coating has the properties desired such as temperature stability, abrasion resistance, cleanability, etc. The electrocoating process is recommended for the speed and relatively low cost of coating.

## CONCLUSION

The IR acrylic system containing Kynar is a decorative material which has been specially formulated so that it may be electrophoretically deposited on a variety of non-conducting and conducting substrates. The IR acrylic system lends itself to accepting an overcoating of Kynar and other fluoropolymers by the IR scheme of electrocoating. Both the acrylic system as well as the polyvinylidene fluoride coating have superb heat resistance and excellent light stability. Because of its excellent durability and cleanliness, it also meets the requirements necessary for decorating of aircraft interiors.

TABLE I

## Preparation of White Conductive FX Resin

	Weight (g) TiO <sub>2</sub>	Weight (g) Al <sub>2</sub> O <sub>3</sub>	Weight (g) AlPO <sub>4</sub>	Weight (g) Cu Powder	Weight (g) POPDA*	Weight (g) Zn Powder	Weight (g) FX Resin		Color After Drying	Conductivity
							Part A	Part B		
1	0.5			0.1			1.1	0.15	Chocolate Brown	None
2	1.0						1.0	0.15	Brownish Pink	None
3	1.0	1.0	1.0				1.0	0.15	Brownish Pink	None
4	2.0	1.0	1.0				1.0	0.15	Pink	None
5	2.0	1.0			0.1		1.0	0.15	Mocha Brown	None
6	1.5					1.0			Gray	Conductive
7	3.0					1.0			Gray	Conductive
8	4.1					1.0			Gray	Conductive
9	3/4 of Mixture 8						1.0	0.1	Pink	Conductive
0	4.5					0.5	1.2	0.15	Pink	Conductive
1						1.5	3.0	0.45	Brown	None
2	20 g. white silicate paint (IR K88-6W)					1.0			Grayish White	None

\*Polyoxypropylene diamine

TABLE II

## Electrocoating With Paints Based on Polyvinyl Salts

Paint Formulation	Substrate	Voltage (volts)	Current (ma)	Time (sec)	Coating Characteristics
PVC IW	Aluminum	100 V	> 500	10	Bubbly, poor adhesion after curing to < 500°F. Above 500°F. coating got charred.
PVC IW	Aluminum	75 V	> 500	10	Bubbly, poor adhesion
3:1 PVC IW : H <sub>2</sub> O	Aluminum	75 V	> 500	10	Bubbly, poor adhesion
PVC IIW	Aluminum	75 V	380	10	Thick, bubbly, poor adhesion
PVC IIW	FRIF, copper-plated	75 V	380	10	Thick, bubbly, poor adhesion
PVA IW	Aluminum	75 V	380	10	Thick, bubbly, poor adhesion
PVA IW + 100 g. H <sub>2</sub> O + 1 drop G.E. Antifoam 60	Aluminum	75 V	380	5	Thin, streaky, bubbly, poor adhesion, heating at 400°F. improved adhesion a little

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TABLE III

## Electrocoating with Epoxy-based Paint Emulsion I, EW

Formulation	Substrate	Voltage (volts)	Current (ma)	Time (sec)	Coating Characteristics	Effect of Curing (212°F.-240°F.)
I EW	Aluminum	200	16	30	Thick, bubbly	Cracked on curing.
I EW + 2 drops Antifoam 66	Aluminum	100	8	30	Thick, fewer bubbles	Cracked on curing.
	Aluminum	100	8	10	Thinner, less bubbles	Cracked on curing.
54 I EW + 50 g. M- Pyrol	Aluminum	100	16	10	Thin, uniform	Remained even and thin.
	Copper-plated FRIF*	100	14	10	Thin, bubbly	Thin, bubbly
	Copper-plated FRIF	100	14	5	Thin, bubbly	Thin, bubbly

\*FX-resin impregnated fiberglass



TABLE IV

## Rate of Electrodeposition of Epoxy-Based Paint

<u>E/D*</u> <u>Time</u> <u>(sec)</u>	<u>Current</u> <u>(ma)</u>	<u>Weight</u> <u>Deposited</u> <u>(mg)</u>	<u>Area</u> <u>Coated</u> <u>(cm<sup>2</sup>)</u>	<u>Thickness</u> <u>(mg/cm<sup>2</sup>)</u>
5	12	16.985	8.46	2.08
5	14	16.697	8.13	2.05
10	14	18.452	8.13	2.27
10	14	19.366	8.64	2.24

Substrate: Aluminum

Curing Temp.: 212°F.

Voltage: 100 volts

Formulation: I EW

\*E/D - Electrodeposition

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TABLE V.

## Electrocoating with Formulation IIEW

Substrate	Voltage (volts)	Time (sec)	Current (ma)	Coating Characteristics
FRIF <sup>1</sup>	125	60	2	No coating
FRIF on Al <sup>2</sup>	125	90	2	Hardly any coating
Aluminum	125	90	2	Hardly any coating
Aluminum	250	90	3	Thin, grainy coating
Aluminum	250	90	3	Thin, grainy coating
FRIF on Al	250	90	5	Thin, even
FRIF on Al	250	120	3	Thin, even, turned yellowish on heating to 350°F. for 10 minutes.
FRIF on Al	250	120	6	Thin, even, rate of deposit was 0.297 g/in <sup>2</sup>
FRIF on Al	300	120	8	Very even

<sup>1</sup>FX-resin impregnated fiberglass (nonconductive)<sup>2</sup>FRIF using the frame

TABLE VI

Electrocoating with Formulation IVER

Substrate: Nonconductive Fiberglass (FRIF) in the Frame

Voltage (volts)	Time (sec)	Current (ma)	Coating Characteristics	Color After 5-minute heating at 400°F.
a 250	60	22	Thin, uniform	Slightly yellow
b 250 <sup>1</sup>	60	22	Thin, uniform	White
c 250	120	22	Uneven	Yellowish
d 200	60	20	Thin, even	Slightly yellow
e 200 <sup>1</sup>	60	18	Thin, even	Very little yellowing, less than d.


  
<sup>1</sup>Recoated with 5% Kynar at 100 volts for 60 sec.

TABLE VII

Electrocoating with Water-Dispersible Epoxy-Based Paint Emulsion

Substrate	Voltage (volts)	Time (sec)	Current (ma)	Coating Characteristics	Effect of Heating
copper-plated FRIF	200	30	450-90	White, gloss" even	15 minutes at 310°F. - no change
FRIF on Al	200	30	450-90	Slightly off-white, even	15 minutes at 310°F. - no change
FRIF on Al 2 coatings	200	30, 15	450-90 90-30	White, thicker, even	15 minutes at 310°F. - no change

TABLE VII

Electrocoating with Water-Dispersible Epoxy-Based Paint Emulsion

Substrate	Voltage (volts)	Time (sec)	Current (ma)	Coating Characteristics	Effect of Heating
copper-plated FRIF	200	30	450-90	White, glossy, even	15 minutes at 310°F. - no change
FRIF on Al	200	30	450-90	Slightly off-white, even	15 minutes at 310°F. - no change
FRIF on Al 2 coatings	200	30, 15	450-90 90-30	White, thicker, even.	15 minutes at 310°F. - no change

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TABLE VIII


## Experiments With Red Epoxy-based Electrocoating Emulsion

Formulation No.	Pigment	Voltage (volts)	Time (sec)	Current (ma)	Substrate	Color of Coating
IER	red iron oxide + ferric acetoacetate	100	60	2	FRIF	Brown
		150	120	4	FRIF coated with white paint*	Yellow
IIER	red iron oxide + ferric acetoacetate	200	120	4	FRIF coated with white paint*	Reddish brown
IIIER	ferric acetoacetate	200	120	6	FRIF coated with white paint*	Yellow
IVER	red iron oxide + molybdate orange	200	120	4	FRIF coated with white paint*	Brownish orange
VER	ferric acetoacetate	200	120	10	FRIF coated with white paint*	Reddish brown
VIER	red fluorescent pigment	250	60	3.5	FRIF coated with white paint*	Melon red

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\*FRIF on which white epoxy-based paint has been electrodeposited

TABLE IX

## Electrocoating with UCAR Latex 891

Substrate	Voltage (volts)	Current (ma)	Time (sec)	Latex Dispersion	Sizing	Coating
Aluminum	300	200	120	L	---	Even, smooth
FRIF* on Aluminum	300	180	15	L	---	Very thin, uneven
FRIF*	300	300	15	PL	yes	TiO <sub>2</sub> plated out of solution very thin coating
FRIF*	300	300	15	PCL	yes	No aluminum deposited with latex, thin coating
Cu-plated FRIF*	200	170	30	PCL	---	Thin coating, bubbly
Fiberglass with FX- resin and aluminum powder	200	30	30	PCLK	---	Uneven, thick
"	200	erratic	30	PCLK	---	Very thin, uneven
" 	250	180	20	PCLK	yes	Uneven; anode smoked after 20 seconds

\*FX-resin impregnated fiberglass

NOTE: curing of coatings was done at 200°F.

TABLE X

Experiments with White Acrylic Electrocoating (Formulation IIIAW)

Substrate	Voltage (volts)	Time (sec)	Current (ma)	Coating Characteristics	Effect of Heating
FRIF on Al	75	10	460-	Very thin	20 min. at 400°F. no discoloration, still tacky
Aluminum	75	10	460	Grainy, thick	1 hr. at 400°F. - no discoloration, still tacky
Aluminum	75	5	460	Uneven	
Aluminum	100	10	460	Thick, slightly grainy	1 hr. at 450°F. - no discoloration, still tacky
Aluminum	100	5	460	Thin, less grainy	1 hr. at 450°F. - no discoloration, still tacky

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TABLE XI

## Electrocoating with Acrylic Formulation VIAW

Substrate	Voltage (volts)	Time (min)	Current (ma)	Coating Characteristics	
				Before Curing	After Curing at 350°F. (5-10 min.)
1 A	200	3	>500-48	Thick, slightly , uneven	Grainy
2 A	150	2	450-12	Very thin	Very thin, uneven on sides
3 A	200	2	450-10	Very thin	Very thin
2 A, recoated	200	2	>500-38	Uneven, thin	Uneven, thin
1 B	200	2	>500-34	Thick on middle part, thin on the two sides	Bubbly, uneven
2 B	200	1	>500-40	Thick, even	Bubbly
1 C	200	1	>500-32	Thick, uneven	Bubbly

- A - FX-resin impregnated fiberglass in the frame  
 B - FRIF sized with 6.7% quaternary ammonium salt  
 C - FRIF sized with 12.5% quaternary

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TABLE XII

## Electrodeposition with Acrylic-Epoxy Crosslink-Based Paint Emulsions

Formulation	Substrate	Voltage (volts)	Time (sec)	Current (ma)	Coating Characteristics (5-minute curing at 350°F.)
AECIW	Aluminum	100	60	500-30	Uneven, tough, white
	Copper-Coated FRIF	100	60	500-0	Even, satin finish, slightly greenish
	Polymide in Frame	100	60	450-44	Uneven, thin, white
AECIIW	Copper-coated FRIF	100	60	100-2	White, very tough, uneven
	Deco Poly-mide with white coating (DPW)	100	60	0	No coating
	DPW in Frame	200	60	>800-16	Thin, even, glossy, mustard stain after 24 hours
	Polyimide in Frame	200	60	>800-15	Very even, glossy, white, became off-white after heating for 10 minutes at 500°F.
AECIIIW	Polyimide in Frame	100	60	>500-30	Even, glossy, white, no mustard stain after 7 days
	Aluminum	100	60	>500-50	Thick, glossy, white

TABLE XIII

Determination of Solvent for Kynar That Will Not  
Affect the Acrylic-Epoxy Crosslink-based Coatings

<u>Solvent</u>	<u>Solubility of Kynar</u>	<u>Solubility of AEC* Coatings</u>
Methyl Isobutyl Ketone	yes	yes
Acetone	yes	yes
Tetrahydrofuran	yes	yes
Methyl Ethyl Ketone	yes	yes
Dimethyl Formamide	yes	yes
Dimethyl Acetamide	yes	yes
Tetramethyl Urea	yes	yes
Trimethyl Phosphate	yes	yes
Diethylene Glycol	yes	no
Polyglycol	no	no
Triethylene Glycol	no	no
Dowanol DB	no	yes
Tributyl Phosphate	yes	yes
Acetonitrile	---	yes
Sulfolane	no	yes
Methyl Jaysolve	---	yes
Ethylene Carbonate	no	---

\*Acrylic-Epoxy Crosslink

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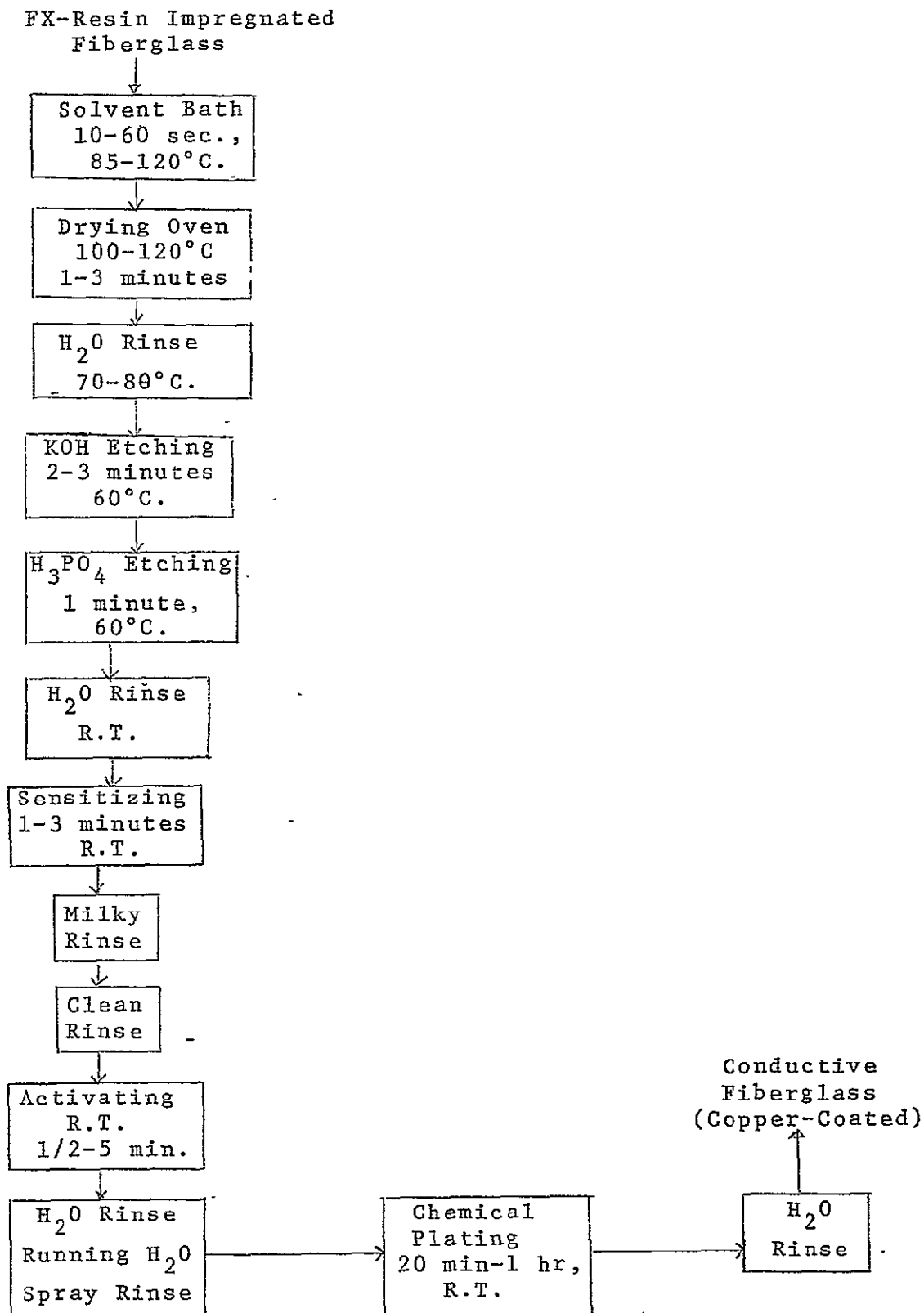
TABLE XIVProperties Data  
IR Acrylic With Kynar

<u>Tests</u>	<u>Results</u>
Taber Abrasion	60-70 mg loss at 1000 cycles, CS10 wheel
Gardner Impact	120 inch pounds direct 160 inch pounds reverse
Pencil Hardness	4 H
Flexibility	Passes 1/4" Mandrel
Adhesion	No failure with 1/16" squares
Scrape Adhesion	No marring with up to 400 gm. load
Detergent Resistance	No failure at 240 hrs. 1% Tide @ 165°F
Water Immersion	No failure or staining after 650 hrs.
Blocking	Non-blocking for 30 minutes @ 82°C. Non-blocking for 24 hours @ 110°C.
Color Fastness to Light	Excellent, non-fading
Cleanability	No discoloration with mustard after 14 days
Crocking	Non-crocking

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FIGURE I

Schematic of Electroless Plating



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Schematic Diagram of Experimental Set-Up

Figure II

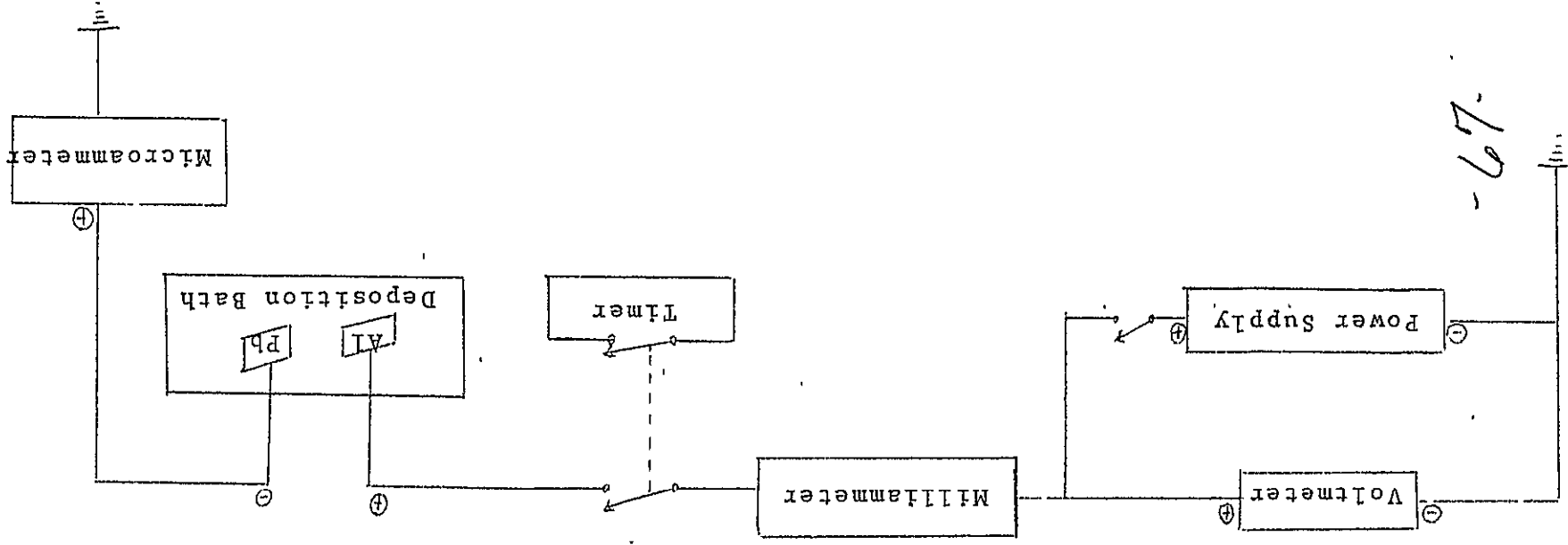
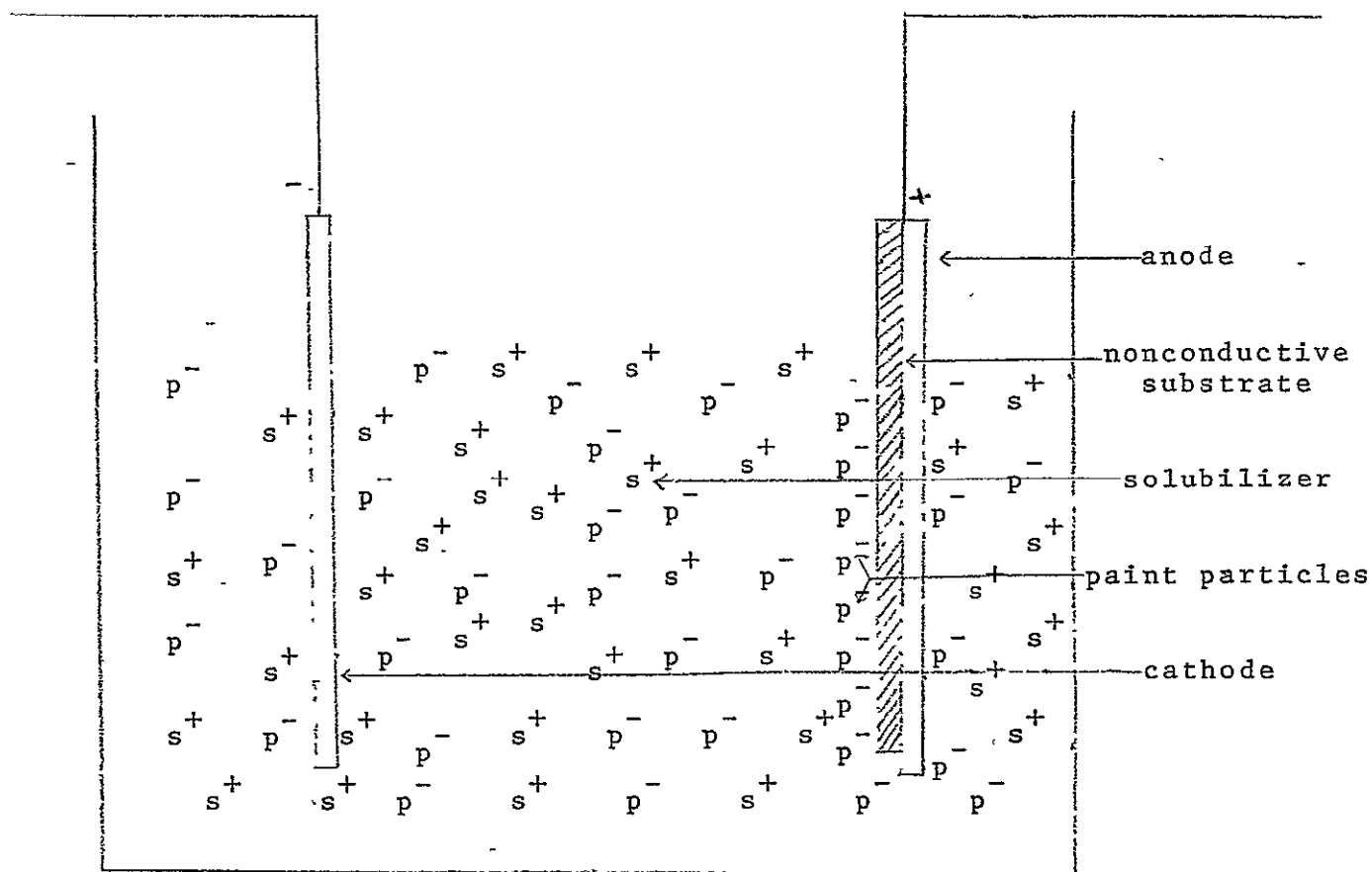


FIGURE III

Principle of Frame Induction Technique



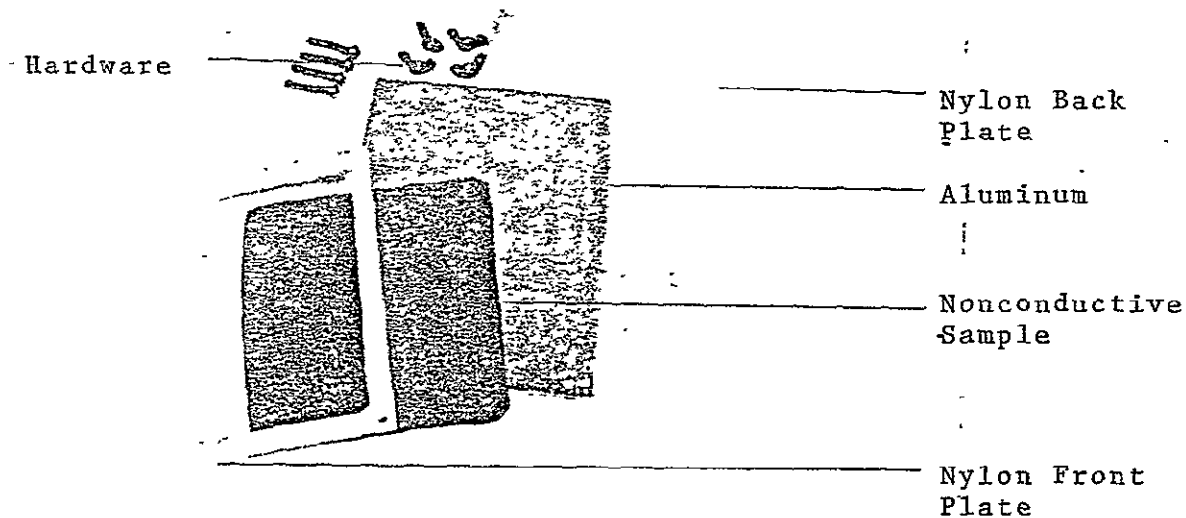
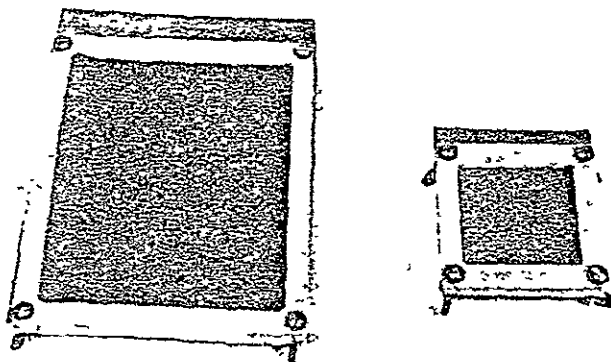


FIGURE IV

Anode Configuration with the Nylon Frame

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FIGURE V. Thermogravimetric Analysis of Polyvinylidene Fluoride

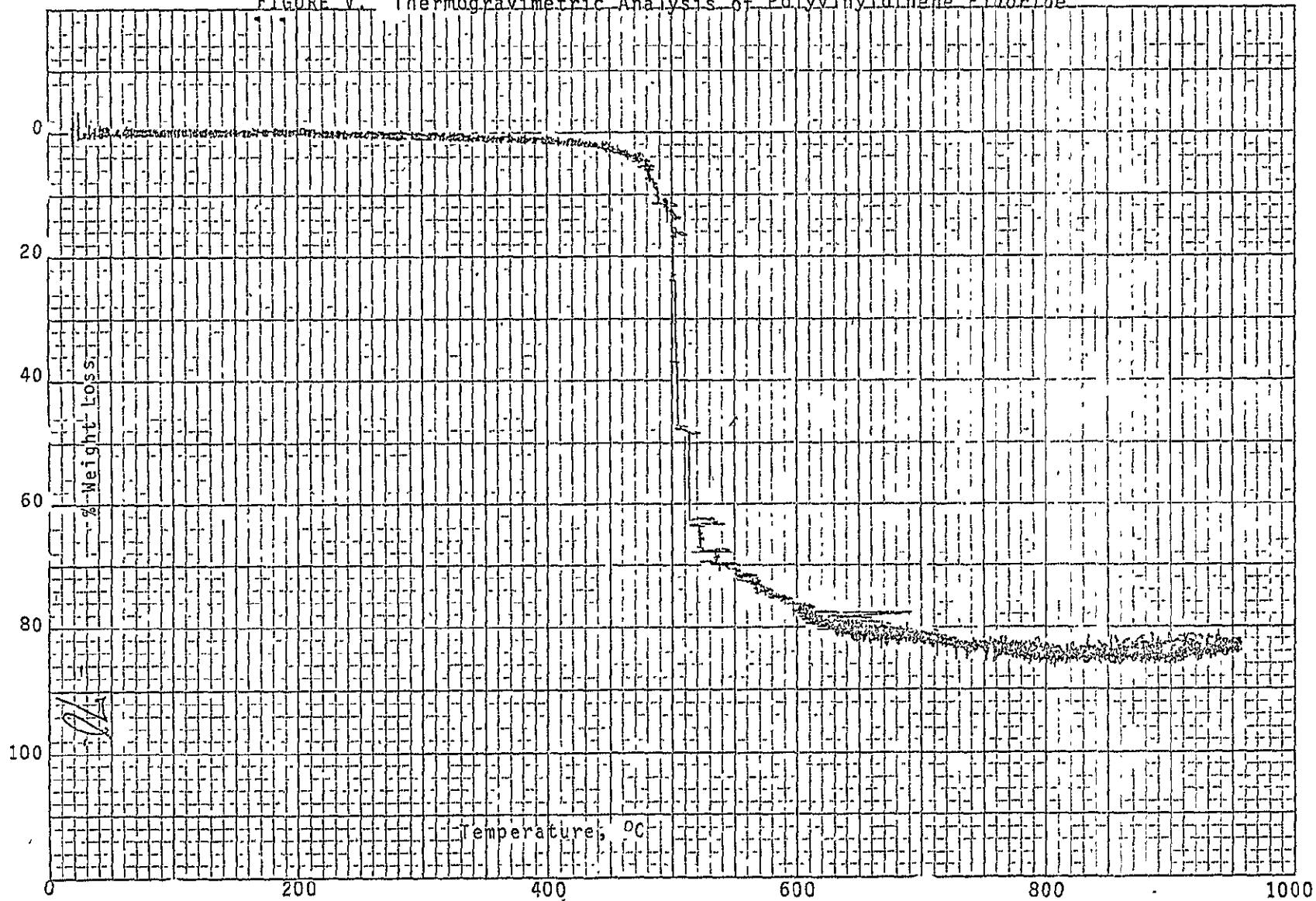


FIGURE VI. Thermogravimetric Analysis of Epoxy Coating with Kynar

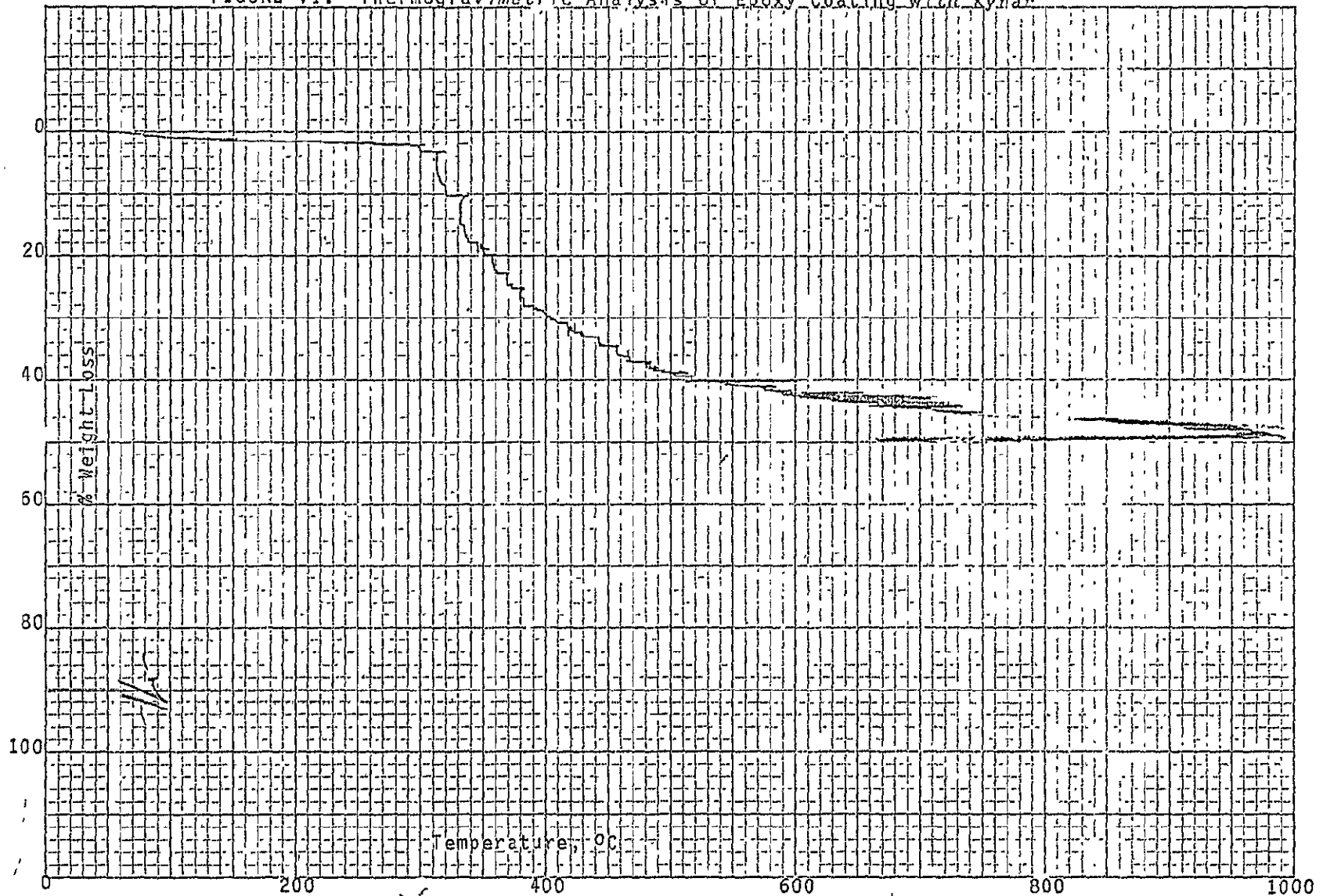


FIGURE VII. Thermogravimetric Analysis of Acrylic Coating

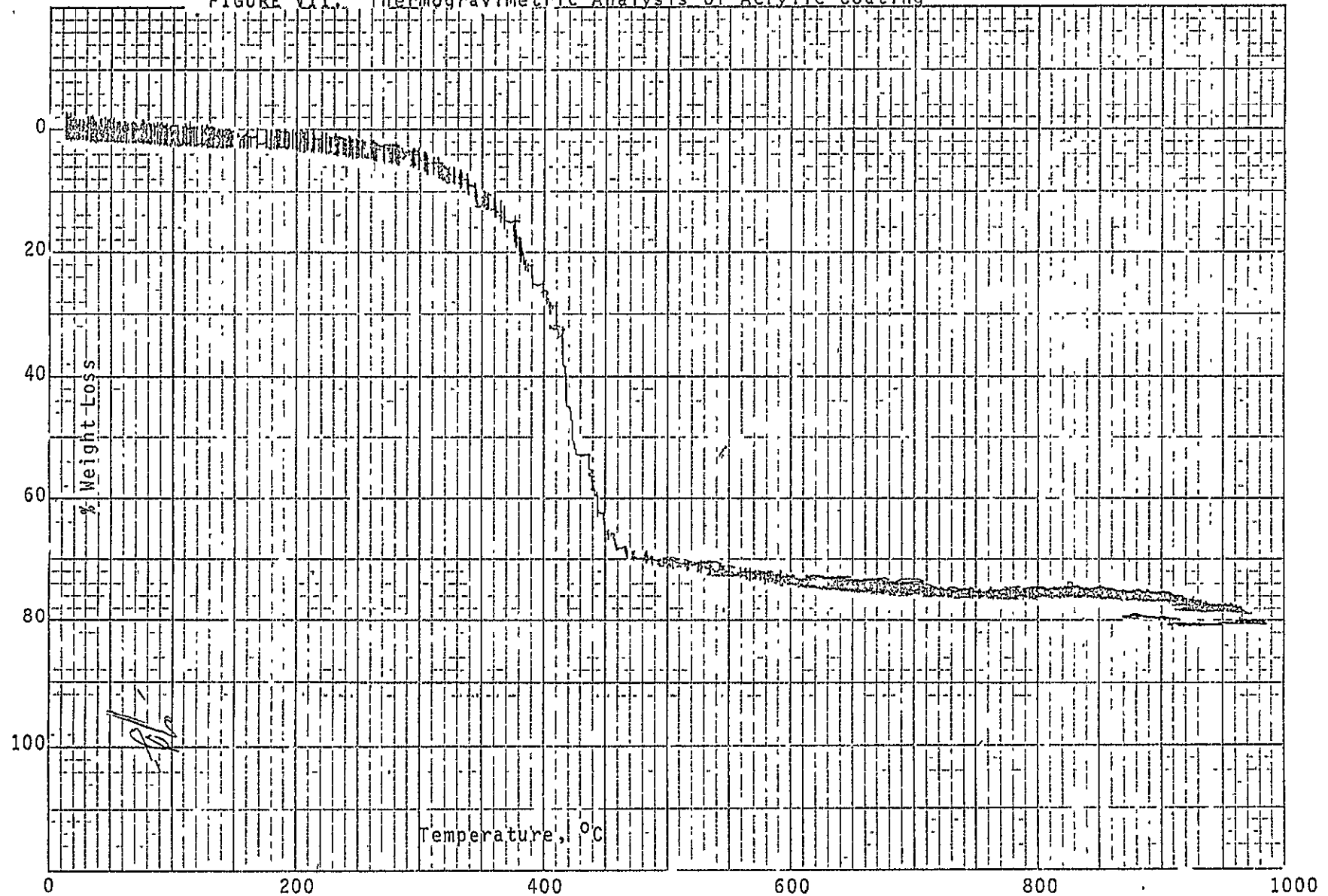


FIGURE VIII Thermogravimetric Analysis of Acrylic Coating with Kynar

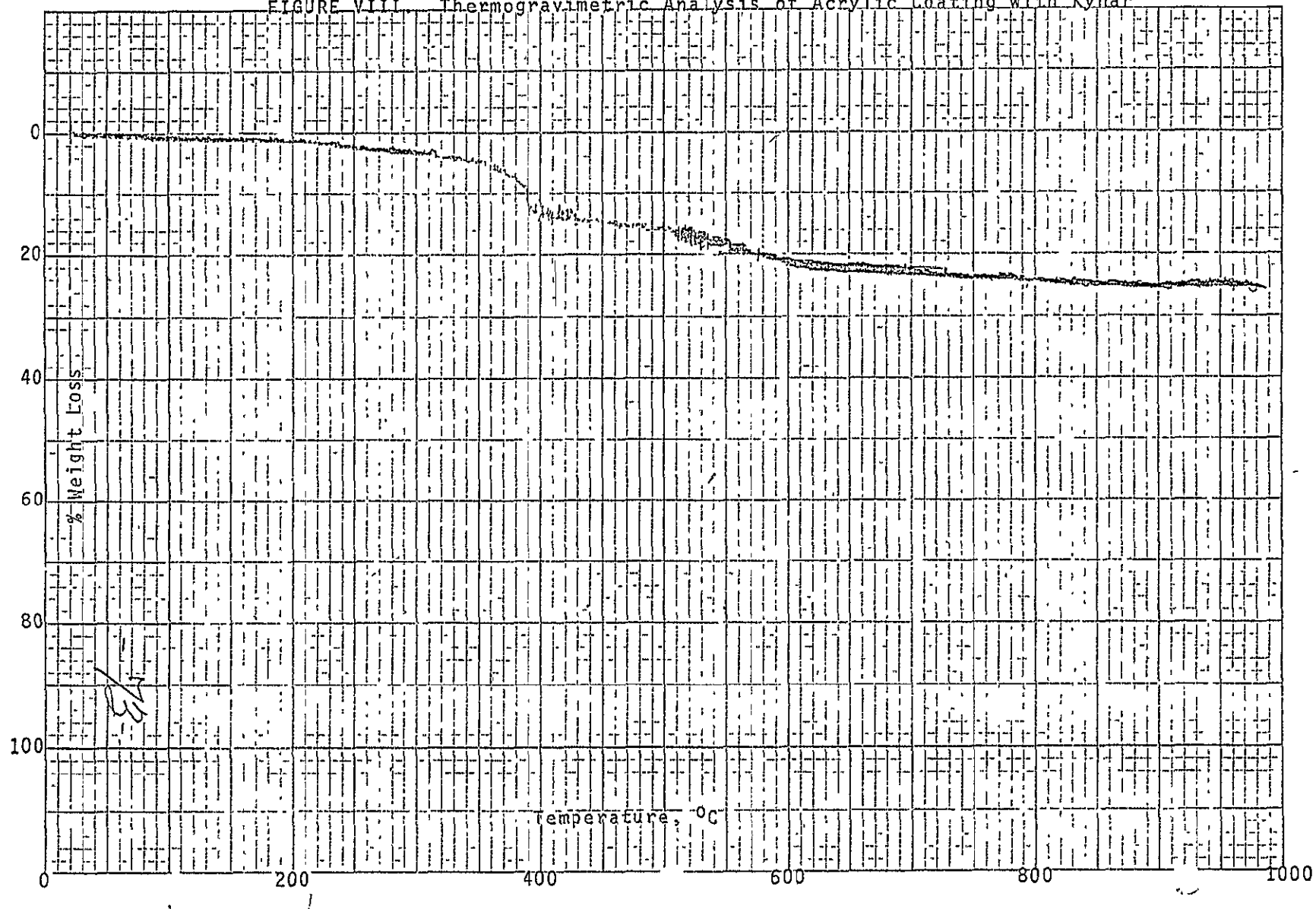


FIGURE IX. Thermogravimetric Analysis of Acrylic-Epoxy Crosslink-based Coating

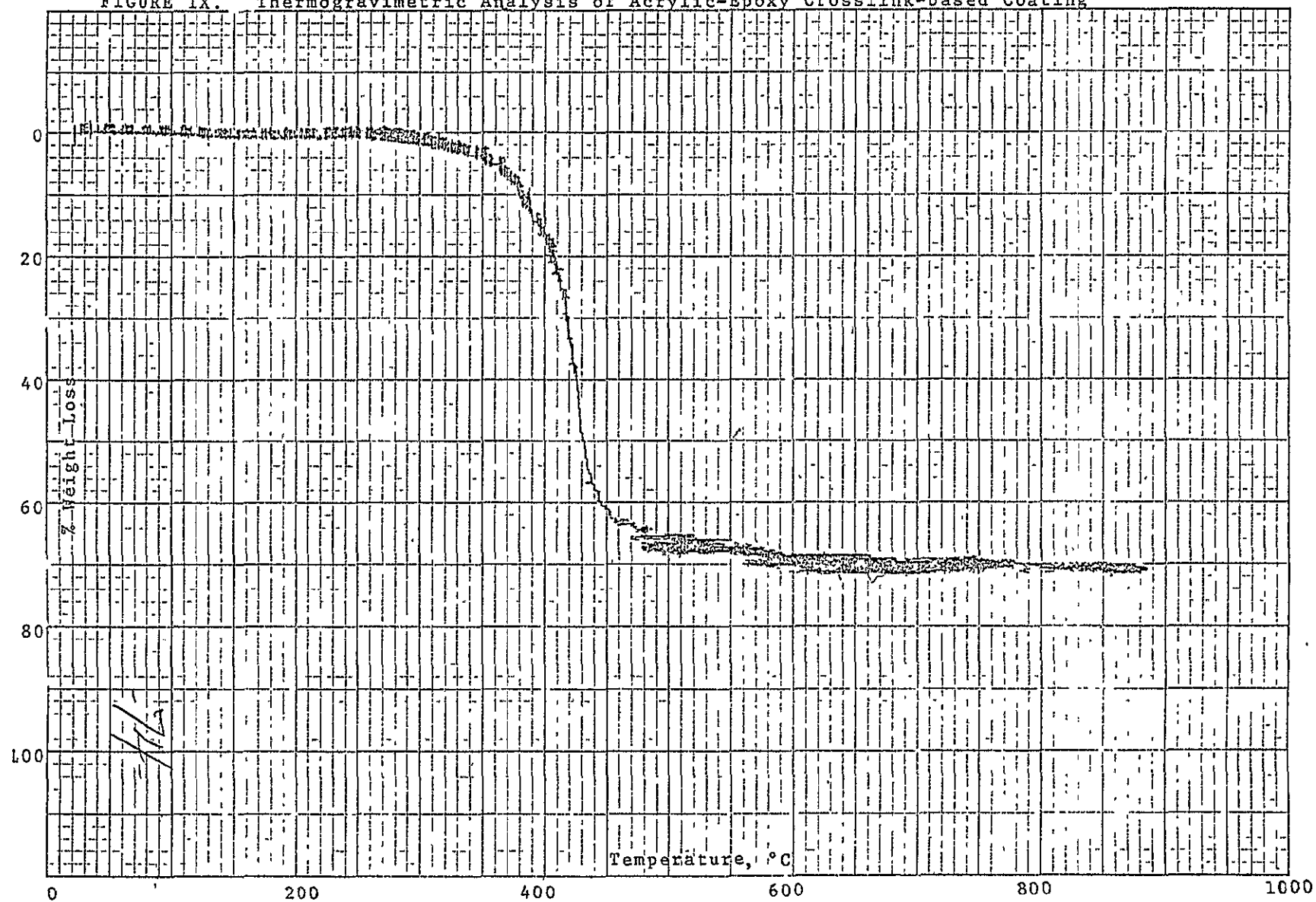


FIGURE X. Thermogravimetric Analysis of Acrylic-Epoxy Crosslink-based Coating with Kynar

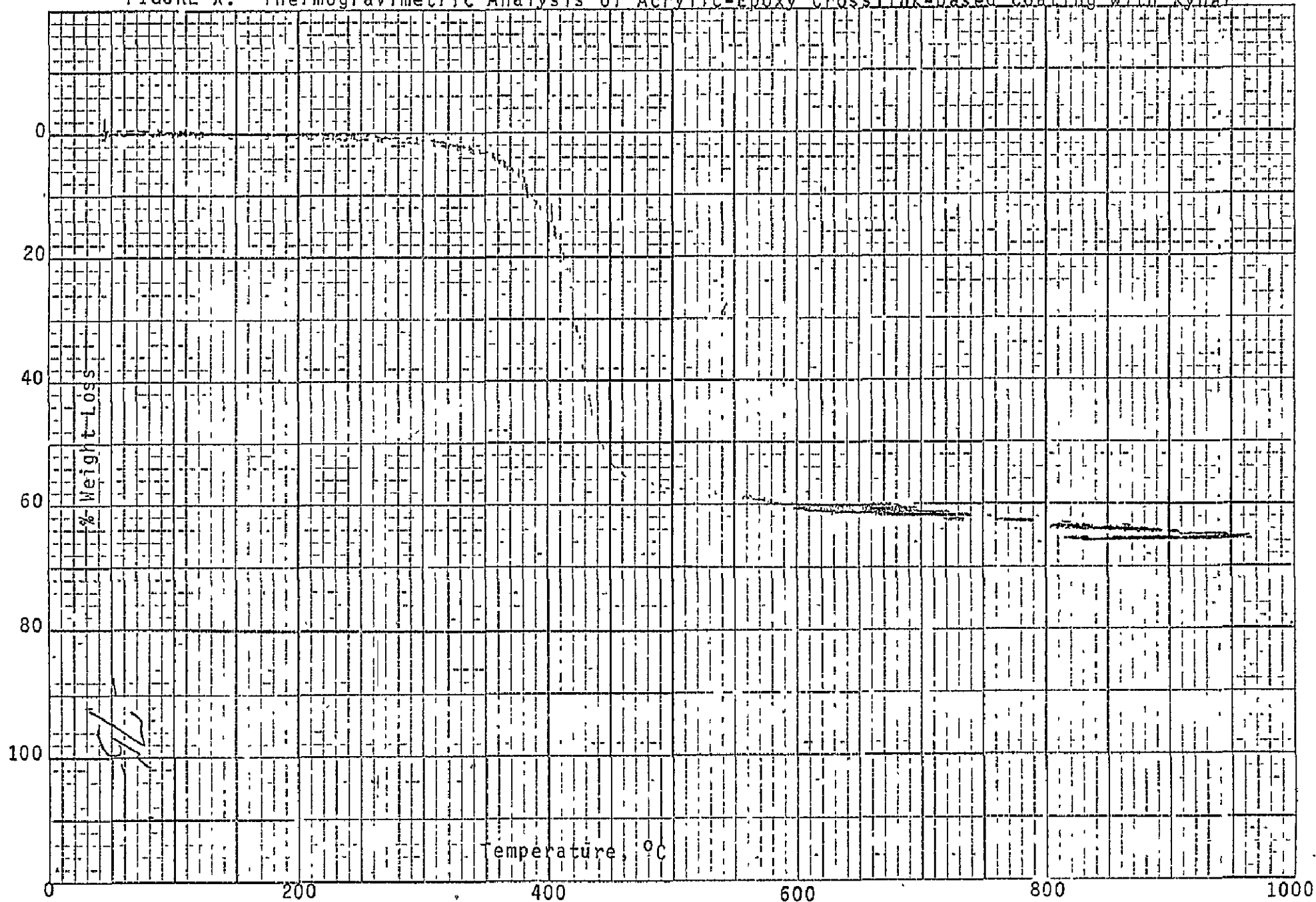


FIGURE XI. Thermogravimetric Analysis of IR 711-16 White Acrylic Coating

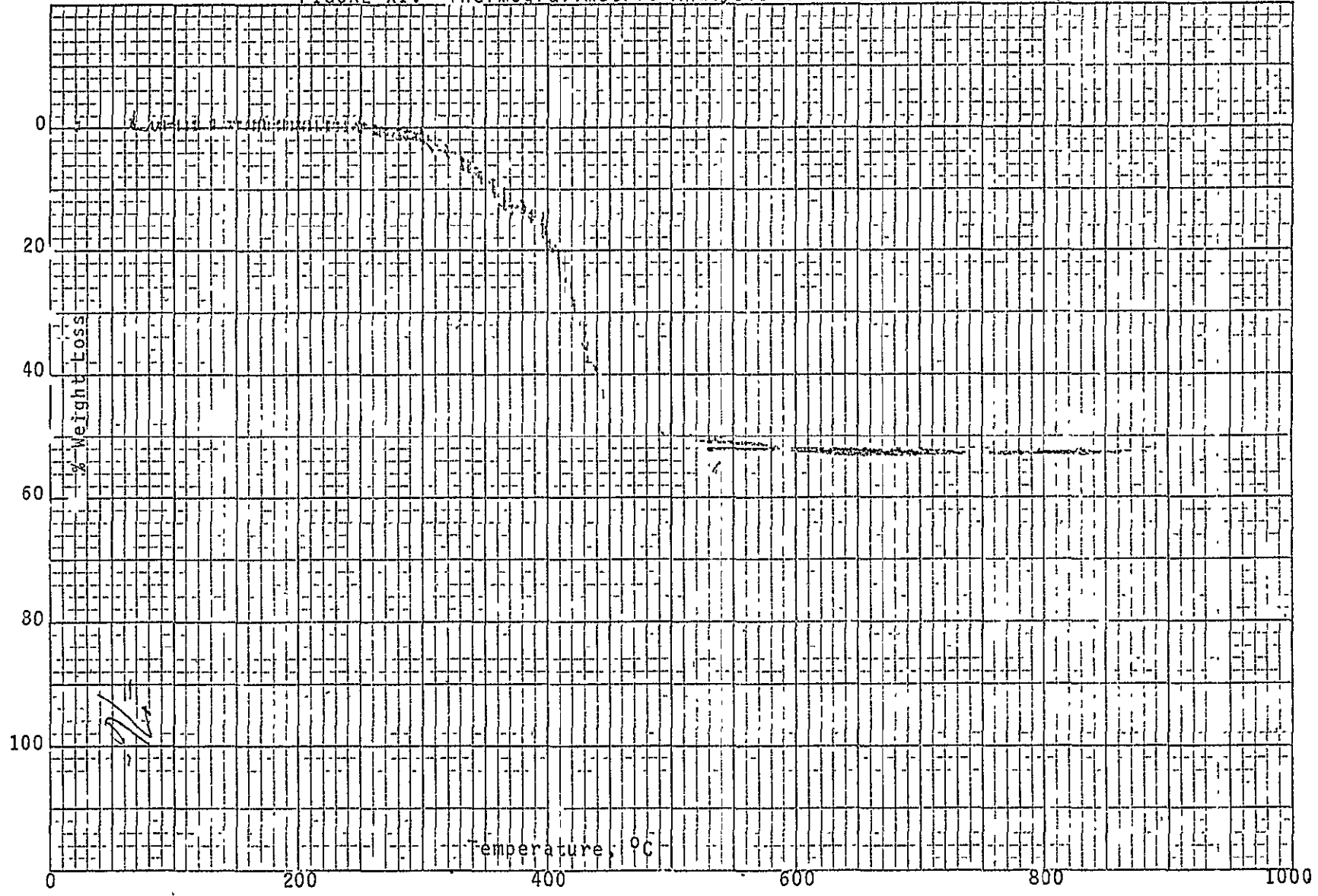


FIGURE XII. Thermogravimetric Analysis of IR 711-16 White Acrylic Coating with Kynar

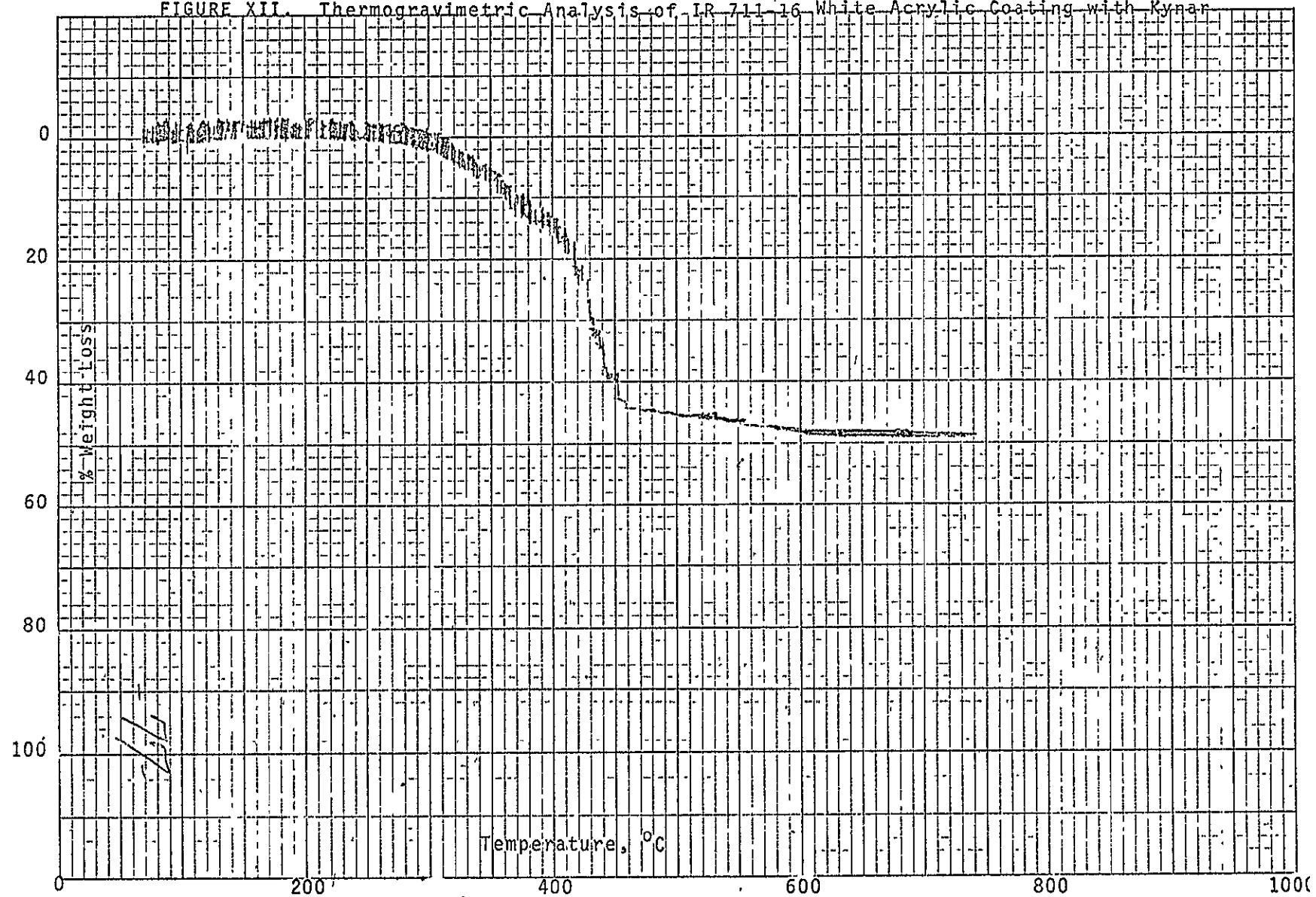




FIGURE XIII. Thermogravimetric Analysis of Gray Acrylic Coating

